Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

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Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

Canada

91-01231/

DEVELOPMENT AND APPLICATION OF ENERGY RECOVERY AND WASTEWATER TREATMENT SYSTEMS FOR SELECTED WASTE STEAMS GENERATED DURING THE PRODUCTION OF FUEL ALCOHOL

PREPARED FOR:

Efficiency and Alternative Energy Technology Branch
Energy, Mines and Resources Canada
Ottawa, Ont.
DSS Contract No. 051SZ.23283-7-6165
September, 1989

PREPARED BY:

CH2M HILL Engineering Ltd.
Suite 600, 180 King Street South
Waterloo, Ont.
N2J 1P8
(519) 579-3500

MICROMEDIA

SCIENTIFIC AUTHORITY:

Jody Barclay
Efficiency and Alternative Energy Technology Branch
Energy, Mines and Resources Canada
580 Booth Street
Ottawa, Ont.
K1A 0E4

93pp

CITATION

Stickney, A.R. and S. Shafai, CH2M HILL Engineering Ltd. Development and Application of Energy Recovery and Wastewater Treatment Systems for Selected Waste Streams Generated During the Production of Fuel Alcohol. Report of Contract File 051SZ.23283-7-6165. Efficiency and Alternative Energy Technology Branch, Energy, Mines and Resources Canada, Ottawa, Ontario. 1989 (79 pp.)

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ACKNOWLEDGEMENTS

The authors would like to acknowledge the following individuals for their assistance in the preparation of this report: Mr. E.N. Hogan, Ms. J. Barclay and the late R.D. Hayes, Energy, Mines and Resources Canada; Mr. E. Yu, Stake Technology Ltd.; Dr. Esteban Chornet, University of Sherbrooke; Mr. Q.A. Nguyen, Forintek Canada Corp.; and Messrs. P. Foody and B. Foody, Iogen Corporation.

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Catalogue No. M91-7/72-1990E
ISBN. 0-662-17567-0

PREFACE

This report is intended to summarize the results of the pilot-scale anaerobic treatability study for treatment of selected wood-to-ethanol waste streams. The report includes a state-of-the-art review of waste treatment technology in the fuel industry and recommendations on the most appropriate waste treatment technology (with emphasis on energy recovery and utilization) for the Steam Explosion Pretreatment Condensate (SEPC) waste stream. Design considerations for full-scale waste treatment systems, projected capital and O&M costs, and estimated revenue/savings for full-scale waste treatment system applications are also included.

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ABSTRACT

The overall objectives of the project were to characterize and assess selected waste streams generated during the processing of sugars derived from lignocellulosic feedstocks to produce fuel-grade alcohol, and to conduct a comprehensive treatability program to develop process standards for waste treatment, with emphasis on energy recovery and utilization. Based on the findings of an extensive literature review and identification and characterization of waste streams generated during the production of fuel alcohol, two waste streams were selected for treatability or toxicity analysis. In selecting appropriate treatment technologies, an emphasis was placed on the potential for energy recovery and utilization.

A Steam Explosion Pretreatment Condensate (SEPC) waste stream was treated anaerobically. Bench-scale Upflow Sludge Blanket (USB) and fixed film anaerobic reactors were used. SEPC was found to be anaerobically biodegradable. COD removals of 80-95% were achieved at 8-10 kg COD/m^3 d organic loadings. Batch anaerobic toxicity assay (ATA) analysis was performed on a lignin recovery waste stream.

Based on the results of the treatability testing, process standards and design criteria were developed for the full-scale implementation of waste treatment technologies. The final report includes process designs, energy balances and economic assessments, including the estimation of the anticipated capital, operation and maintenance costs.

It was estimated that the income from the utilization of the biogas as a fuel is significantly lower than the estimated total operating cost: as a result, no payback in the wastewater treatment system would be anticipated.

At the request of Energy, Mines and Resources Canada, a poster was prepared by CH2M HILL describing the objectives, methodology and results of the project. This poster was presented at the Seventh Canadian Bioenergy R&D Seminar in Ottawa, April 24-26, 1989.

RÉSUMÉ

Le projet avait pour objectifs généraux de caractériser et d'évaluer les déchets liquides produits lors du traitement des sucres contenus dans la matière lignocellulosique servant à produire de l'alcool à combustion et de réaliser un programme de traitement complet dans le but d'élaborer des normes de traitement des déchets de bois, dans une perspective de récupération de l'énergie et son utilisation. Après avoir effectué une étude approfondie de l'information existante et avoir analysé le genre de déchets provenant de la production d'alcool à combustion dans le cas présent, deux types de déchets furent choisis dans un but d'analyse de possibilités de traitement et de toxicité. Le choix d'une technique appropriée de traitement visait surtout la récupératiuon de l'énergie et son utilisation.

Les rejets composés de condensats produits par explosion à la vapeur furent traités dans des conditions anaérobie. Pour cette expérience, on a utilisé à échelle d'essai un courant ascendant de lie de boues et des réacteurs anaérobie à pellicule fixe. Les condensats se sont révélés biodégradables en milieu anaérobie. La suppression de 80 à 95 % de la demande chimique en oxygène a été réalisée à 8-10 kg DCO/m^3 j de charge organique. On a également réalisé des analyses de toxicité anaérobie par lot sur les déchets servant à la récupération de la lignine.

Les résultats des essais de traitement ont permis d'élaborer des normes de traitement et des critères de conception pour la mise en oeuvre à grande échelle de la technologie du traitement de déchets de bois. Le rapport définitif comprend une description de la méthode, des tableaux d'équilibre énergétique et des évaluations financières comprenant le coût d'investissement prévu et les frais d'opération et d'entretien.

1.0 INTRODUCTION AND BACKGROUND

1.1 Introduction

This project was initiated by Energy Mines and Resources Canada to provide wastewater characterization and treatability data and to estimate capital and operating costs for the treatment and disposal systems for wastewater resulting from the production of fuel alcohol.

1.2 Background

The production of ethanol for human consumption from fruits, vegetables and grain dates back to the earliest of times. It was not until the nineteenth century, however, that ethanol was used as fuel. In the 1830's, ethanol became a popular fuel to replace malodorous fish and whale oils for lighting. In 1906, the United States Congress passed the Industrial Denatured Alcohol Act which removed the tax on alcohol for industrial purposes to encourage the use of ethanol. Ethanol-alcohol blends were also used in France as early as 1907, and in the United States in the 1920's ethanol became a popular farm fuel.

It was not until World War I, however, that ethanol was produced on a commercial-scale from wood. Between 1910 and 1922, two full-scale plants were in operation in the Southern United States producing 19,000 to 26,500 litres of 95 percent ethanol per day from wood. Several plants were also constructed in Europe during that period based on a Wood-to-Ethanol conversion process developed in the 1920's in Germany by Heinrich Scholler.

During the period following World War I, more efficient petroleum-refining techniques were developed which resulted in higher quality and cheaper gasoline. This led to a decline in the popularity of alcohol fuels until the Depression and the advent of prohibition in the United States. These events caused an excess of agricultural produce on the European and North American markets, which again led to the promotion of ethanol as fuel.

During World War II, ethanol was also used extensively due to a shortage in the supply of petroleum-based fuels. Following the war, however, gasoline and diesel fuel became

readily available again, which led to a decline in the popularity of alcohol fuels.

The energy crisis in the 1970's renewed the interest in the use of alcohol fuels. At that time, it was anticipated that new cars and new fuels would be developed, and that the dependence on foreign oil suppliers would be ended. The 1980's, however, brought a prolonged oil glut and a drop in oil prices.

Recently, there has been another resurgence of interest in alcohol fuels initiated by environmental concerns over air pollution levels. The Canadian and American Governments have embarked on a program to significantly reduce the level of lead emissions from North American automotive exhaust by the late 1980's. The replacement of this octane enhancer with ethanol is being tested with very positive results in both Canada and the United States.

Currently in North America, fuel ethanol is only being produced at full-scale from grain. A considerable amount of work is being conducted at laboratory and pilot-scale to develop a commercial-scale process to convert ligno-cellulosic feedstocks to ethanol. Lignocellulosics are abundant in Canada and they are a much cheaper feedstock than grain and sugar products.

Ferguson (1987) reported that current estimates show that the availability of forest biomass in Canada is in the order of 100 million dry tonnes per year, which is equivalent to approximately 25 percent of Canada's total primary energy demand.

Approximately 29,500,000 litres of gasoline are consumed in Ontario every day. For every one percent replacement of gasoline, 295,000 litres of fuel alcohol per day or 108 million litres per year are required. It is estimated that 900 million litres of ethanol would be required per year in Canada if ethanol/methanol was used as the only octane enhancer and if ethanol was blended with gasoline at a rate of three percent.

The production of large volumes of ethanol would also result in the generation of large volumes of waste products that would require treatment. When ethanol is produced from grain, the major waste products remaining are the distillery by-products, including the distiller's dry grains (DDG) and

solubles (DDS). These by-products may be dried and used as animal feed.

A full scale alcohol replacement program would not be feasible unless DDG is utilized. However, if fuel alcohol production were made feasible without DDG utilization, by government incentive or technological advancement, it is anticipated that there will be an excess of these by-products that will require waste treatment and disposal.

A summary of the quantity of distillery by-products that may be consumed daily by various livestock animals is shown in Table 1.1. Table 1.2 summarizes the number of animals required to utilize the stillage generated from a 1,000,000 litre per year Ethanol-from-Corn fuel alcohol plant.

Table 1.1
CONSUMPTION RATE OF DISTILLER'S DRIED GRAIN BY VARIOUS LIVESTOCK

Type of Animal Production	Production Rate	Feed		Stillage (L/d)	
		Conventional Feed (kg/d)	DDG (kg/day)	10% Solids	20% Solids
250 kg Calf (hay ration)	0.9 kg gain/day	6.2	2.6	23.8	11.7
350 kg Steer	1.3 kg gain/day	8.8	3.9	34.8	17.4
590 kg Cow	22.7 kg/day, 3.5 percent milk	16.8	3.0	27.3	13.6
30 kg Pig	0.6 kg gain/day	1.5	0.5	4.5	2.3
Pullets Age 3.7 Weeks		0.06	0.06	NA	NA
Pullets Age 7.5 Weeks		0.10	0.10	NA	NA

NA = Not Applicable
Table prepared by CH2M HILL

Table 1.2
ESTIMATED NUMBER OF ANIMALS AND LAND BASE REQUIREMENT TO SUPPORT A 1,000,000 LITRE/YEAR FUEL ALCOHOL PLANT

Livestock	DDG Consumption (kg/head.d)	Number of Animals Required to Utilize By-product	Land Base Required to Utilize By-products as Fertilizer (Ha)	Land Base Required to Utilize Annual Manure Production (Ha)
Beef, 250 kg	2.6	770	1,100	385
Beef, 350 kg	3.7	540	1,100	360
Beef Cow, 550 kg	3.0	667	1,100	667
Pigs, 30 kg	0.5	4,000	1,100	1,200

Table prepared by CH2M HILL

A considerable amount of research work has been conducted on the characterization and treatability of the waste streams generated from the production of ethanol from grain (Stover 1983, 1984; Lanting et al, 1985). A full-scale anaerobic system has also been installed at South Point Ethanol in Ohio to treat the waste streams generated from the plant. The system is described in detail by Johnston et al, (1987).

When ethanol is produced from wood, several waste products are generated. The characteristics and volumes of these waste streams depend on the conversion process and the type of wood used. The still bottoms or stillage remaining after fermentation is the major waste product generated. A wide variety of figures have been reported for the volume of stillage generated during the production of ethanol from wood. B.H. Levelton and Associates (1983) reported stillage production levels of 10 litres of stillage per kilogram of dry wood processed. Callander et al (1986) determined that 20.4 litres of stillage were generated per kilogram of dry wood from the pilot-scale Wood-to-Ethanol process at the Forest Research Institute in New Zealand and Strickland et al (1986) reported figures in the range of 5.8 litres of stillage per kilogram of dry wood for the Wood-to-Ethanol pilot-scale conversion process at the Tennessee Valley Authority (TVA) in the United States. Other waste streams generated during the production of ethanol from wood include condensates from pretreatment processes, lignin and undigested cellulose.

1.3 Objectives

The overall objectives of this project were to characterize and assess the waste streams generated during the processing of sugars derived from lignocellulosic feedstocks to produce fuel grade alcohol, and to conduct a comprehensive treatability program to develop process standards for waste treatment, with emphasis on energy recovery and utilization.

The specific objectives were as follows:

1. To identify and characterize the waste streams generated during the production of fuel grade alcohol from wood feedstocks.

2. Based on the waste stream characterizations, to evaluate and select appropriate wastewater treatment technologies (with emphasis on energy recov-

ery and utilization) for each waste stream, and identify waste streams that require further treatability analysis.

3. To prioritize and perform selected wastewater treatability studies on the identified waste streams.

4. To develop process standards and design criteria for the full-scale implementation of waste treatment technologies for the selected waste streams including process designs, energy balances and economic assessments.

5. To prepare a comprehensive report summarizing the results of the treatability studies and of the energy and economic assessment including an example process design, capital, and operation and maintenance costing.

2.0 WOOD-TO-ETHANOL CONVERSION PROCESS

2.1 Conversion Process Description and Waste Stream Identification

Wood is composed mainly of cellulose, hemicellulose and lignin. The percentage of each of the components is dependent upon the type of wood, as shown in Table 2.1. Cellulose is composed entirely of six carbon sugars and it is a homogeneous polymer of glucose. Hemicellulose is composed of five and six carbon sugars. It may contain polymers of hexoses (glucose, galactose and mannose) and pentoses (xylose and arabinose). Lignin consists of cross-linked polymers of phenyl propane units joined by benzylic and phenolic ether linkages. The remaining fraction of wood is composed of materials such as ash, resin, oils, polysaccharides and volatile acids.

Table 2.1
BASIC COMPOSITION OF WOOD

	Polysaccharides			
	Cellulose (% by Wt.)	Hemicellulose (% by Wt.)	Lignin (% by Wt.)	Extractives (% by Wt.)
Softwoods	45	15 - 20	25 - 30	<10
Hardwoods	45	20 - 30	15 - 20	<10

Source: (B.H. Levelton & Associates, 1983)

The Wood-to-Ethanol process generally involves pretreatment, hydrolysis, fermentation and distillation. A schematic of the various process alternatives for the production of ethanol from wood is presented in Figure 2.1.

The conversion of wood to ethanol is dependent upon the chemical characteristics of the cellulose, hemicellulose and lignin fraction contained in wood. Wood must be pretreated either by grinding, treatment with dilute acid or by steam explosion to break down the wood and render the substrate amenable to the subsequent hydrolyzation stage. When wood is hydrolyzed, either by acid or enzymatic hydrolysis, the cellulose fraction breaks down into 6-carbon sugar units

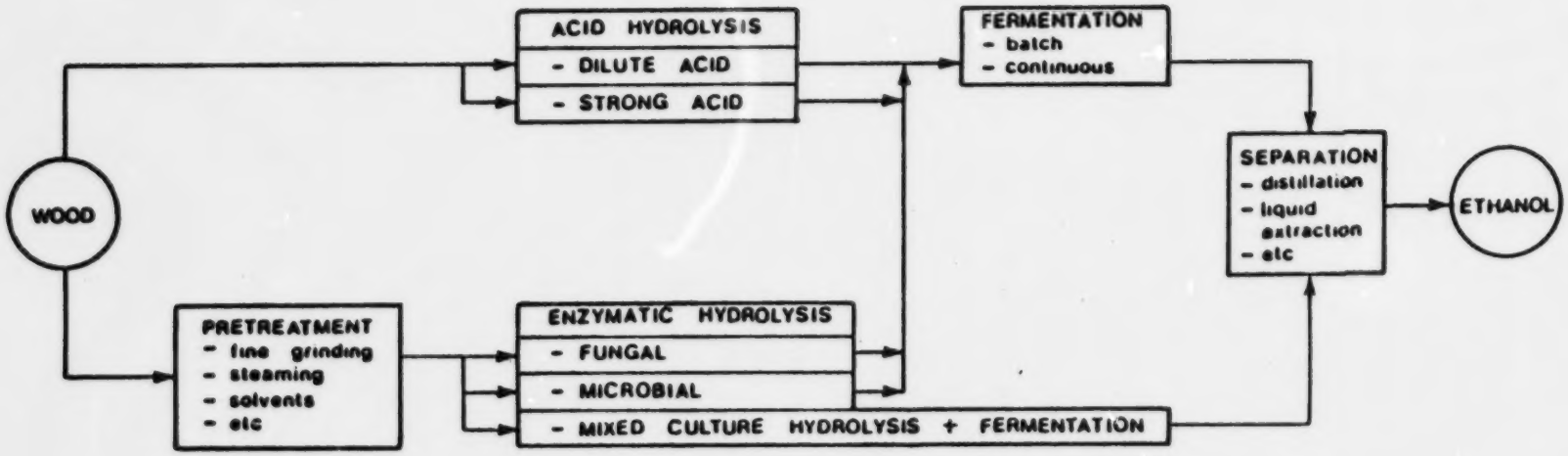


Figure 2.1 Alternate Processing Routes to Ethanol from Wood

(hexosans) and the hemicellulose forms mainly 5-carbon (pentosans) and some 6-carbon sugars. The lignin and remaining fraction of wood do not break down to sugars, but form complex compounds.

All of the Canadian Wood-to-Ethanol pilot plant processes being studied only utilize the hexosan sugars from the cellulose fraction as the substrate for the fermentation stage.

Laboratory and pilot-scale work are currently being conducted to develop yeast strains that are capable of fermenting the pentosan sugars to ethanol. It is estimated that pentosan fermentation could increase the total ethanol yield by up to one third.

2.1.1 Pretreatment Processes

Lignocellulosic feedstocks must undergo a pretreatment process to render the material more amenable to subsequent conversion processes. The wood may be pretreated by mechanical particle size reduction, solvent extraction, dilute acid prehydrolysis, or steam explosion. Only dilute acid hydrolysis and steam explosion will be discussed further in this section, as these are the only two pretreatment processes being tested in Canadian pilot-scale Wood-to-Ethanol systems.

The dilute acid prehydrolysis process consists of breaking down the hemicellulose, cellulose and lignin fractions by the addition of dilute acid, typically sulfuric acid. The objective of dilute acid prehydrolysis is to remove easily hydrolyzed hemicellulose sugars to more readily isolated pure glucose streams.

Steam explosion involves the high pressure steaming of lignocellulosic materials to break down the hemicellulose, cellulose and lignin bonds and to increase the surface area to render the components more accessible to the hydrolyzing agents introduced in the subsequent hydrolysis process.

The major waste product generated from this process is the waste steam. This waste steam may be condensed and the condensate treated in liquid form. The characteristics of the condensate are dependent upon the wood type and steam explosion process conditions. Steam treatment renders cellulose more reactive, which potentially results in a higher hexose yield, however, it also causes the degradation of cellulose and hemicellulose. Cellulose degrades to form hydroxymethyl

2 - furfuraldehyde and hemicellulose degrades to form furfural, which may react further with the lignin fraction. Other compounds that may be contained in steam explosion pretreatment condensate (SEPC) include acetic acid, from the decomposition of the hemicellulose fraction, and methanol. Traces of formaldehyde, acetaldehyde, vinyl acetate, 2 - methoxyethyl acetate, phenol and furfural methyl ketone may also be present, depending on the process conditions. Some of these compounds, especially furfural and acetic acid, may be recovered through steam stripping or centrifugation, however, the economic feasibility may not warrant the installation of a recovery system and these compounds may have to be treated.

2.1.2 Lignin Extraction

Lignin may be separated from the sugar solution either before or after the hydrolysis process. Typically lignin is recovered by solvent extraction using either aqueous ethanol, dioxane or butyl alcohol. The solvent is usually recovered and reused and lignin is the only remaining product.

2.1.3 Hydrolysis

The hydrolysis process is accomplished by the introduction of either acid or enzymes to obtain the greatest yield of fermentable sugars while minimizing the decomposition of the glucose as it is formed during hydrolysis.

Acid hydrolysis is accomplished either with dilute acids at elevated temperatures (approximately 240°C) or with strong acid at low temperatures (approximately 20°C). Hydrochloric, sulfuric or gaseous anhydrous hydrochloric acids are typically used, and other acids, such as hydrofluoric acids, are being investigated. Dilute acid hydrolysis has been more widely applied, although both processes have been applied commercially.

B.H. Levelton and Associates (1983) reported that there are no commercial or near-commercial processes for the enzymatic hydrolysis of forest biomass to sugars. A considerable amount of research, however, is being conducted to develop a commercial-scale system because it has been demonstrated that up to 95% of the wood cellulose may be converted to glucose with the process. These yields are considerably higher than those obtained with acid hydrolysis processes.

The process equipment would also be considerably less costly and energy consumptive because the process proceeds at low temperatures (approximately 50°C) and atmospheric pressure.

During the production of the enzyme, the enzyme solution must be centrifuged or passed through an ultra-filtration system to recover the enzyme cake. The centrifuge centrate or permeate, which may contain fungus cells and nutrients, is considered a waste product.

2.1.4 Fermentation

The fermentation process consists of the conversion of the sugars resulting from the hydrolysis process to alcohol and carbon dioxide. Only the simple hexose sugars, such as glucose, fructose, mannose and galactose, may be fermented with the commonly-used yeast, Saccharomyces cerevisiae, to produce ethanol.

The pentosan or five-carbon sugars are not fermented by Saccharomyces cerevisiae, and pass through the fermentation process and end up in the remaining stillage. A considerable amount of research is being conducted on the fermentation of the pentose sugars because of the potential to greatly increase the ethanol yield.

The characteristics of the still bottoms product or stillage remaining after fermentation is very dependent upon the process conditions and the products fermented. Typically stillage contains some form of undigested cellulose and pentosans if they have not been removed and fermented separately.

3.0 LITERATURE REVIEW

There is very little information available in the literature on the characteristics or treatability of waste streams generated during the production of ethanol from lignocellulosic feedstocks. The Tennessee Valley Authority (TVA) in Muscle Shoals, Alabama, the Solar Energy Research Institute (SERI) in Golden, Colorado, the Forest Research Institute (FRI) in Rotorua, New Zealand and the Forschungsabteilung EMS-INVENTA wood saccharification plant in Domat/EMS Switzerland have all been involved in the characterization and anaerobic treatability studies of the still bottoms product, or stillage, remaining after distillation.

3.1 Tennessee Valley Authority (TVA)

R.C. Strickland et al (1986a) identified the principal effluents generated from the TVA's Ethanol-from-Hardwood project and estimated the volumes of generated effluents. The TVA Wood-to-Ethanol process consists of a two ton per day pilot plant, which uses locally available mixed hardwood chips. The first stage in the process involves hydrolysis pretreatment with dilute sulphuric acid at high temperatures, followed by a second stage hydrolysis with weak acid, then bulk fermentation and distillation.

A summary of the effluents identified from the TVA process is presented in Table 3.1.

Table 3.1
EFFLUENTS GENERATED FROM THE TVA's
ETHANOL-FROM-HARDWOOD PROCESS

Solids	Liquids	Gases
Gypsum	Stillage	Fermentation Off-Gases
Residual	Concensates	Flash Vapours
Lignocellulose	Fusel Oils	Boiler Flue Gases
Boiler Ash	Sanitary Wastewater	
Excess Yeast	Boiler Blowdown Water	
Dust		
Bark & Wood Waste		

Source: Strickland et al, 1986a

A summary of TVA estimates of mass flows and volumes for a plant processing 100 tons of dry wood per day is presented in Table 3.2.

Table 3.2
ESTIMATED MASS FLOWS AND VOLUMES FOR MAJOR EFFLUENTS FOR A PLANT PROCESSING 100 TONNES DRY WOOD/DAY

	First Stage	Second Stage	Total
Gypsum (t/day)	2.8	4.1	6.9
CO_2 (t/day)	8.0	8.9	16.9
Residual Lignocellulose (t/day)	-	18.8	18.8
Stillage - Organic Matter (t/day)*	8.5	17.1	25.6
- Volume (m^3/d)	241.1	290.3	531.4
Condensates - Organic Matter (t/day)	0.4	0.3	0.7
- Volume (m^3/d)	13.3	70.9	84.2

* Excludes furfural and acetic acid steam stripped from hydrolyzate and sugar remaining after fermentation.
Source: Strickland et al, 1986a

The emphasis of Strickland et al (1986a) work was on the characterization of the stillage remaining after distillation and an assessment of the potential for, and problems associated with the anaerobic digestion of this waste stream.

A summary of the TVA's second-stage hardwood stillage characteristics is presented in Table 3.3.

The anaerobic treatability studies were conducted in a six litre reactor seeded with five litres of sludge from the Muscle Shoale wastewater treatment plant. The reactor contents were mixed for forty-five minutes per hour and allowed to settle for fifteen minutes. At the end of the settling period, fresh stillage was added at an initial daily feeding rate of 1 kg COD/m^3·d.

Table 3.3
SUMMARY OF THE TVA PROCESS STILLAGE CHARACTERISTICS

Parameter	
Chemical Oxygen Demand (mg/L)	19,100
Total Solids (mg/L)	22,900
Volatile Solids (mg/L)	18,500
Total Nitrogen (mg/L)	2,800
Sulphate (mg/L)	900
Phosphate (mg/L)	74
Calcium (mg/L)	2,210
Iron (mg/L)	48
Chromium (mg/L)	12
Nickel (mg/L)	25
Acetic Acid (mg/L)	800
Levulinic Acid (mg/L)	1,500
Residual Sugar (mg/L)	<100

Source: Strickland et al, 1986a

Results from the TVA's work suggested that the stillage was amenable to anaerobic digestion at low COD loading rates in a stirred tank reactor. Strickland et al (1986b) estimated that the methane produced from the anaerobic digestion of stillage had an energy equivalent of 27.1 gallons of ethanol/ton wood processed or 14.3 percent of the total wood energy. It was suggested that the methane could be marketed or used to replace part of the lignin that is used in the conversion process as fuel.

Further research on anaerobic digestion at the TVA was to include studies on microbial acclimation to second-stage stillage and an evaluation of methane production from first-stage stillage and mixtures of first and second-stage stillage.

A second area of co-product research at TVA involved the identification of higher value non-fuel uses for the residual lignocellulose from the process (Strickland et al, 1986b). The work involved aspects of delignification and the physical and chemical characterization of lignin. Efforts were being directed toward adhesive applications because of the large market potential. Other research has included the use of lignin as a slow release agent in the production of fertilizer.

3.2 Solar Energy Research Institute (SERI)

The Solar Energy Research Institute (SERI) has also been involved with the conversion of biomass to fuel. Rivard et al (1985) compared the use of a standard completely stirred tank reactor with upflow packed bed reactors to produce methane by anaerobically digesting hydrolysate from the acid pretreatment of wheat straw.

Currently, research and development efforts at SERI are being concentrated on the problems associated with the pretreatment of wood, and wastewater studies are being given a lower priority.

3.3 The Forest Research Institute (FRI)

FRI has also been involved in stillage characterization and anaerobic treatability studies (Callander et al 1986a, 1986b and 1987).

The FRI Wood-to-Ethanol process uses softwood chips, sawdust or shavings. The softwood feedstock is firstly hydrolyzed with dilute acid at high temperatures. The resulting hot acidic sugar solution is cooled and then neutralized with lime, filtered, fermented and distilled to produce pure ethanol. It is estimated that approximately 18 tons of ethanol are obtained from 100 oven dry tons of wood and that approximately 22 litres of stillage are generated for every 1 litre of ethanol produced (What's New In Forest Research, 1985).

Callander et al (1986a) characterized the stillage from the FRI process. The results of the characterization study are presented in Table 3.4.

Callander et al (1986a) also conducted an extensive literature review of the degradability by methanogenic consortia of aromatic compounds associated with the degradation of carbohydrates and lignin. It appears that only m-cresol, o-cresol, vanillic acid and veratric acid are incompletely degraded. A literature review of the inhibiting concentrations of carbohydrates and lignin degradation products and associated compounds to anaerobic bacteria was also conducted. A summary of the inhibiting concentrations is presented in Table 3.5.

Table 3.4
SUMMARY OF THE FRI PROCESS STILLAGE CHARACTERISTICS

Parameter	Average Value (mg/L)
Chemical Oxygen Demand	25,500
5-Day Biochemical Oxygen Demand	13,200
Total Solids	13,700
Volatile Solids	8,800
Suspended Solids	400
Total Nitrogen	95.3
Total Phosphorus	10.3
Total Sulphur	600
Aluminum	2.93
Calcium	1,110
Cobalt	<0.04
Chromium	4.10
Copper	0.62
Iron	146
Potassium	38.5
Magnesium	27.2
Sodium	172
Nickel	8.9

Source: Callander et al, 1986a

Table 3.5
INHIBITING CONCENTRATIONS OF CARBOHYDRATE AND LIGNIN DEGRADATION PRODUCTS AND ASSOCIATED COMPOUNDS TO ANAEROBIC BACTERIA

Compound	Inhibiting Concentration (g/L)	Acclimated Culture
Furfural	>0.58, <1.16	No
	>0.50	Yes
	1.7	No
	>2.32, <5.78	Yes
	>3.0	Yes
5-Hydroxymethyl furfural	1.7 - 2.1	No
Laevulinic Acid	8.1 - 11.5	No
Reductic Acid	4.8	No
Phenol	2.44 (50% inhibition)	Yes
Catechol	2.64 (50% inhibition)	Yes
Guaiacol	>1.1, <5.6	No
	2.2	No

Source: Callander et al, 1986a

The results of FRI's initial stillage characterization study and theoretical investigation of the amenability of the stillage to anaerobic digestion indicated that the stillage is mainly comprised of organic compounds consisting of unfermented pentose sugars and a variety of carbohydrate and lignin degradation compounds. It was postulated that many of these degradation products may be inhibitory to anaerobic bacteria, however, based on reports of related compounds, it was speculated that all compounds should be anaerobically biodegradable. The low concentrations of nitrogen and phosphorus observed in the stillage indicated that the supplementation of these nutrients would be required for stable anaerobic digestion. The high sulphur concentration indicated that inhibition problems may result, but the concentrations of other inorganic nutrients appeared to be at levels that would not be inhibitory to the anaerobic digestion process.

Following the initial stillage characterization work, FRI conducted anaerobic treatability studies. The objectives of their work were to develop anaerobic biomass acclimated to Pinus radiata stillage, quantify the nutrient, mineral and alkalinity requirements and assess the efficiency of the anaerobic digestion process under conditions of increased loading rate.

An 8 litre continuously-mixed reactor, maintained at 37°C, was used in the initial study. The pH was maintained above 6.8 using caustic and $NH_4H_2PO_4$, KCl, $MgCl_2.6H_2O$ and $FeCl_3.6H_2O$ were added as sources of the nutrients (nitrogen, phosphorus, potassium, magnesium and iron). The sulphate concentration of the stillage was reduced from 1800 mg/L to 500 mg/L with barium chloride to more closely approximate sulphate concentration from commercial-scale processes. The sulphate remaining in the stillage is a function of the temperature at which the hydrolysis liquor is neutralized. In the FRI process, the liquor is neutralized at 80°C and in commercial-scale units it can be neutralized at 140°C, decreasing the sulphate concentrations.

The reactor was fed at an initial loading rate of 1.0 kg COD/m^3·d and gradually increased to 4.0 kg COD/m^3·d.

The results of the study indicated that stable operation could be obtained at organic loading rates up to 4.0 kg COD/m^3·d and that COD removal rates of 90 percent could be attained. It appeared that the addition of potassium, magnesium and iron was not necessary. Nitrogen and phosphorus

were added at the rates of 9.1 x 10^{-2} g/g VSS synthesized and 3.3 x 10^{-2} g/g VSS synthesized, respectively. The alkalinity addition was 4 mL of 20 percent NaOH/L stillage. It was noted that sulphate removal may be required to avoid propionate accumulation.

Further anaerobic digestion studies were conducted at FRI to assess the suitability of a USB reactor for stillage (Callander et al, 1986b). A 10 litre USB reactor, maintained at 37°C, was used in the study. The reactor was seeded with 6 litres of acclimated sludge and 4 litres of effluent from the completely-mixed reactor used in the previous study. The reactor effluent was recycled at a rate of approximately five times the flow rate of the influent stillage. Nitrogen, phosphorus and caustic were supplemented at the rates of 240 mg N/L stillage (9.4 mg N/g COD), 120 mg P/L stillage (4.7 mg P/g COD) and 2.5 - 5.0 mL 20 percent NaOH/L stillage fed, respectively. The sulphate concentration was also reduced to 500 mg SO_4^{2-}/L, as in the previous study, to more closely approximate sulphate levels in stillage from commercial-scale plants. The organic loading rate was gradually increased, and after 98 days of operation a loading rate of 16 kg COD/m^3·d was attained.

The results of the study indicated that organic loading rates of 16 kg COD/m^3·d could be attained with soluble BOD and COD removal levels of 93 percent and 86 percent, respectively, and methane production yields of 0.302 L CH_4/g COD removed.

At higher loading rates than 16 kg COD/m^3·d, inhibition was observed. Only the addition of nitrogen, phosphorus and caustic was required.

3.4 Forschungsabteilung EMS-INVENTA

Good et al (1982) conducted laboratory-scale anaerobic treatability studies with stillage remaining after the fermentation of eucalyptus wood chips at the Forschungsabteilung EMS-INVENTA wood-saccharification plant in Domat/Ems, Switzerland. The Wood-to-Ethanol pilot-scale process involves the hydrolysis of wood chips with hot dilute sulphuric acid. The hydrolyzate is then neutralized and fermented. The substrate used in the treatability studies consisted of stillage mixed with an equal part of treated effluent from a laboratory-scale fixed film anaerobic reactor. The diluted substrate characteristics are listed in Table 3.6.

Table 3.6
SUMMARY OF THE FORSCHUNGSABTEILUNG EMS-INVENTA WOOD-SACCHARIFICATION PLANT DILUTED SUBSTRATE CHARACTERISTICS

Parameter	
Chemical Oxygen Demand (mg/L)	22,500
Total Solids (mg/L)	17,600
Volatile Solids (mg/L)	15,600
Ash (mg/L)	2,000
Total Sulphur (mg/L)	260 - 360
Total Nitrogen (mg/L)	200
Total Phosphorus (mg/L)	40
pH	5.8 - 6.3
COD:N:P	1000:8.8:1.7

Source: Good et al, 1982

The treatability trials were conducted with a 2 litre completely stirred tank reactor (CSTR) and 0.45 litre fixed film reactors containing stainless steel wire mesh support structures with a specific area of 4 cm^2/cm^3 of reactor volume. The results of the treatability trials are summarized in Table 3.7.

Table 3.7
SUMMARY OF THE PERFORMANCE OF THE FIXED FILM AND CSTR REACTORS AT FORSCHUNGSABTEILUNG EMS-INVENTA

Parameter	Fixed Film Reactor		CSTR
	Mesophilic Operation (35°C)	Thermophilic Operation (55°C)	Mesophilic Operation (35°C)
Hydraulic Retention Time (days)	2.1	2.25	9.5
Organic Loading Rate (kg COD/m^3·d)	10.7	10	2.4
COD Removal (%)	86.6	84.4	85.5
Specific Biogas Production (m^3/kg COD)	0.40	0.38	0.40
CH_4 Content (%)	63.4	62.5	58.5
H_2S Content (%)	0.01	0.01	0.01
Effluent Volatile Acids:			
Acetic Acid (mg/L)	260	215	532
Propionic Acid (mg/L)	680	666	1900
Temperature (°C)	35	55	35
pH	7.5	7.2	7.3

Source: Good et al, 1982

The results of the study indicated that stable operation was attained with both the fixed film and CSTR reactor systems, but much higher organic loading rates could be attained with the fixed film reactors. It was also observed that total reactor influent sulphur concentrations of 8 - 11 mM resulted in the maximum organic loading rates. Sulphur concentrations greater than 16 mM, however, resulted in decreased methane production and pH.

3.5 Pulp and Paper Industry

Apart from the anaerobic treatability studies conducted on stillage, no other information on Wood-to-Ethanol process waste stream characterization or treatability work was found in the literature. A literature review of the characterization and treatability work done in the pulp and paper industry was conducted to determine whether any of the work done in that field was applicable to the Wood-to-Ethanol industry.

A considerable amount of characterization and treatability work has been conducted with evaporator condensates from sulphite and Kraft chemical pulping processes in the pulp and paper industry.

3.5.1 Sulphite Process

Sulphite Evaporator Condensate (SEC), which originates from the vapours produced on evaporation of spent sulphite liquor, is quite similar in composition to the condensate generated during the pretreatment of wood by steam explosion (SEPC) in some Wood-to-Ethanol processes. The characteristics of SEC vary widely from one pulp and paper mill to the next depending on the type of wood used, the dilution factor of the wash and the type and efficiency of the chemical processes. Generally SEC, like SEPC, contains high concentrations of acetic acid, methanol and furfural. A comparison between the characteristics of SEC from various sources is presented in Table 3.8.

Benjamin et al (1982) conducted treatability studies with SEC from a calcium bisulphite mill and with synthetic SEC. Four 18.5 L submerged media anaerobic reactors (SMAR) were started up at a loading rate of 1 kg COD/$m^3 \cdot d$. Failures were observed at low alkalinity levels and without the addition of nutrients, but toxicity from sulphur compounds, furfural and trace organics did not appear to be a problem.

Table 3.8
COMPARISON BETWEEN SULPHATE EVAPORATOR CONDENSATE (SEC) CHARACTERISTICS
FROM VARIOUS SOURCES

	Benjamin et al (1982)		Benjamin et al (1984)	Brune et al (1982)	Walters et al (1988)	Qiu et al (1987)	Saslawsky et al (1988)		Donovan et al (1984)
	Industrial SEC	Synthetic SEC					Preliminary Study	Recent Study	
COD (mg/L)	5000	5000	4000 - 7000	10000 - 20000	4000 - 8000	1202	7500	6000	8250 - 16300
Acetic Acid (mg/L)	3000	3000	3750	6000 - 24000	3000	-	2000 - 3000	4000	4700 - 11500
Methanol (mg/L)	800	1000	730	-	250	421	2000	500	760 - 1130
Furfural (mg/L)	400	-	225	500 - 3000	250	-	1200	700	930 - 2300
$SO_{2(aq)}$ as S (mg/L)	250	-	-	640 - 1280	1500	-	600	25	
Ethanol (mg/L)	-	-	100	-	-	5.8			
Propionic Acid (mg/L)	-	-	150	-	-	-			
Butyric Acid (mg/L)	-	-	50	-	-	-			
Formic Acid (mg/L)	-	-	-	-	500				

Nitrogen and phosphorus were added at the rates 7.2 kg/1000 kg COD removed and 0.9 kg/1000 kg COD removed, respectively, and a loading rate of 16 kg COD/m^3·d was achieved.

Berg and Eder (1985) reported the findings of anaerobic treatability studies of SEC with a 6 m^3 USB reactor. The condensate consisted primarily of organic acids and contained an average of 15,000 - 20,000 mg COD/L and 9,000 - 12,000 mg BOD_5/L. The wastewater was diluted with water to 8000 mg COD/L at start-up and the COD:N:P ratio was maintained at 350:5:1. A loading rate of 9.0 kg COD/m^3.d was achieved with COD and BOD_5 removal efficiencies of 80 percent and 90 percent, respectively. The process design for a full-scale treatment plant producing 160 ton/day bleached sulphite pulp and 410 ton/day of tissue napkin and toweling products, was also presented. The plant was designed to treat 1400 m^3/d of wastewater with an average COD of 16,800 mg/L and an average BOD_5 of 10,500 mg/L. An organic loading rate of 8.8 kg COD/m^3·d was used, resulting in a reactor volume of approximately 2,600 m^3. The treatment system included a stainless steel heat exchanger to cool the condensate, a 560 m^3 surge tank for flow equalization, a 38 m^3 nutrient and pH adjustment tank, a 460 m^3 sludge storage tank, gas handling equipment consisting of a compressor, after-cooler, dryer and flare system, and the process instrumentation and controls. The estimated cost of the system was $US 3.5 million with annual operating and maintenance costs of $US 359,000.

Maxham and Dubey (1984) evaluated anaerobic and aerobic technologies to treat SEC from a calcium based sulphite pulp mill. The SEC had an average COD concentration of 14,300 mg/L and a pH in the range of 1.7 to 2.9. The composition of the SEC used in the study was not reported.

A nutrient mixture containing 1.34 g NH_4Cl/L, 0.42 g K_2HPO_4 L, 0.19 $MgSO_4.7H_2O$/L, and 0.042 g $CaCl_2.2H_2O$/L was added to the SEC to compensate for the nutrient deficiencies. Approximately 10 mL of 15 N NaOH was also added to the SEC to bring the pH up to between 4.5 and 7.0 depending on the technology being tested.

Different experimental set-ups were used in the study. Experiment 1 was conducted with 3.88 litre USB reactor. During the experiment, COD removal efficiencies of up to 80 percent were obtained. However, the highest organic loading rate achieved was only approximately 1 kg COD/m^3·d. In experiment 2, a 5.08 litre aerobic activated sludge unit was

tested. BOD and COD removal efficiencies of 99.8 percent and 98 percent, respectively, were obtained at a loading rate of 3.1 kg COD/m^3·d. The aerobic sludge flocculated well, but it could not be concentrated to greater than 7 g VSS/L, and therefore, higher loading rates than 3.1 kg COD/m^3·d could not be achieved. In experiment 3, the aerobic and anaerobic reactors used in the two previous experiments were combined. BOD and COD removal efficiencies of 99.9 percent and 98 percent respectively, were achieved at an organic loading rate of 5.0 kg COD/m^3·d. A COD removal efficiency of 97.5 percent was obtained when the loading rate was increased to 7.5 kg COD/m^3·d.

Donovan et al (1984) conducted an anaerobic pilot study with SEC from an ammonia based sulphite mill. Three anaerobic technologies, an anaerobic filter, a USB and a fluidized bed, were evaluated. The characteristics of the SEC are listed in Table 3.8. Donovan et al reported that loading rates in the range of 25 to 50 kg COD/m^3·d were achieved with the fluidized bed reactor, 15 to 20 kg COD/m^3·d with the anaerobic filter and 4 to 5 kg COD/m^3·d with the USB at COD removal efficiencies of 80 percent or greater. Specific biogas production rates in the range of 0.46 to 0.54 m^3/kg COD removed were reported at these loading rates, with biogas methane contents of approximately 70 percent.

Brune et al (1982) also conducted anaerobic treatability studies with SEC. Twelve 10 L, completely mixed, reactors were used in the study. Stable operation was attained at a loading rate of 1.7 kg COD/m^3·d. The loading rate was increased to greater than 6.8 kg COD/m^3·d by recycling the biomass by external sedimentation or filtration. A nutrient mixture was added to each litre of condensate, as summarized in Table 3.9.

The furfural and sulphur compounds contained in the SEC did not inhibit digestion.

3.5.2 Kraft Process

Benjamin et al (1983) examined the anaerobic toxicity and biodegradability of pulp mill waste constituents. A series of anaerobic toxicity assays (ATA) and biological methane potential (BMP) tests were conducted with SEC to determine the biodegradability and inhibiting effects of furfural, guaiacol, p-cymene, eugenol, limonene and difurfuryl disulfide. The results of the ATAs and BMPs conducted with furfural indicated that concentrations of 1,160 mg/L of

Table 3.9
NUTRIENT MIXTURE FOR ANAEROBIC TREATMENT
OF SULPHATE EVAPORATOR CONDENSATE

Macro-Nutrient Mixture

0.5 g NH_4Cl

0.6 g $MgCl_2.6H_2O$

0.25 g $CaCl_2.2H_2O$

0.2 g NaCl

1.5 mg $FeCl_2$

3 mL Mineral-1

13 µL Mineral-2

1 g $Na_2HPO_4.2H_2O$

0.8 g $NaH_2PO_4.2H_2O$

Mineral - 1	Mineral - 2
(stock solution/L)	(stock solution/L)
0.475 g $MnCl_2.4H_2O$	2 g $Na_2 SeO_3.5H_2O$
0.17 g $CoCl_2.6H_2O$	2 g $Na_2 WO_4.2H_2O$
0.050 g $CuSO_4.5H_2O$	2 g $Na_2 Mo_4.5H_2O$
0.18 g $ZnSO_4.7H_2O$	
0.018 g $Alk(SO_4)_2.12H_2O$	
0.01 g H_3BO_3	

Source: Brune et al, 1982

furfural were toxic to unacclimated organisms, but that concentrations of 5,780 mg/L were not inhibitory to acclimated organisms. It was observed that with acclimated organisms, the furfural was not inhibitory and readily degraded.

Brune et al (1983) conducted a study with SEC to isolate a strictly anaerobic bacteria which used furfural as the sole source of carbon and energy. The furfural isolate was identified as Desulfovibrio sp. strain F-1.

Full-scale anaerobic plants have also been constructed to treat evaporator condensates from pulp and paper mills. Walters et al (1988) described a full-scale SEC treatment system at a 70,000 ton per year bleached pulp mill in the Federal Republic of Germany. A volume of 1,600 m^3/d of high strength SEC is produced with COD concentrations ranging from 4,000 mg/L to 8,000 mg/L. The treatment system consists of a steam stripping tower to remove the sulphur dioxide, a 2,155 m^3 anaerobic contact reactor, a 10 m^3 biogas storage tank, a sedimentation tank and an aeration tank. The organic loading rate to the anaerobic reactor was approximately 5 kg COD/m^3·d and COD and BOD_5 removal efficiencies of 77 percent and 96 percent respectively, were being achieved. A waste product from a local manufacturing plant was added as a source of nitrogen, phosphorous, iron, cobalt, zinc, lead, tin and chromium. Several mechanical and operational problems were experienced during the start-up, but they were mainly associated with the acclimation of the microorganisms in the anaerobic reactor. Seed sludge from an anaerobic reactor at a sugar mill did not adapt well to the SEC, however, sludges from reactors treating brewery waste and sludge from a municipal treatment plant adapted well.

Saslawsky et al (1988) reported the results of the operation of a full-scale, 2,550 m^3 fixed film anaerobic reactor and a 5 m^3 pilot-scale fixed film anaerobic reactor treating SEC at a 400 MT/d bleached pulp plant in Tartas, France. The characteristics of the SEC are presented in Table 3.8. The full-scale system consists of a nutrient and trace mineral addition tank, a heat exchanger, a 2,550 m^3 stainless steel, upflow fixed film reactor packed with 3 inch polypropylene PALL rings and biogas handling and utilization equipment.

Several problems were experienced with the full-scale facility and the reactor had to be re-seeded three times after the initial start-up. The reactor was initially seeded with municipal sewage sludge, then re-seeded with municipal

sludge, sludge from an anaerobic reactor treating distillery waste and finally sludge from an anaerobic system treating potato waste. The maximum organic loading rate attained was 3.0 kg COD/$m^3 \cdot d$, which is only 50 percent of the design load. The organic loading rate was decreased to 2.5 kg COD/$m^3 \cdot d$ after the reactor was re-seeded with sludge from an anaerobic system treating potato waste. Cheese whey was added as a source of nutrients at the rate of 10 percent of the COD fed. As a result, the COD removal efficiency increased from 65 percent to 80 percent. The 5 m^3 pilot-scale reactor, containing 1.5 inch PALL rings, was also re-seeded with potato processing sludge and an organic loading rate of 5.5 kg COD/$m^3 \cdot d$ was achieved with stable operation. The much higher organic loading rate, achieved with the pilot-scale reactor as compared to the full-scale reactor, was thought to be associated with the clogging problems in the full-scale system.

Nitchals et al (1985) used a 20 L submerged media anaerobic reactor (SMAR) to conduct anaerobic treatability trials with condensates from Kraft (KEC) and acid sulphite (SEC) processes. Caustic extraction (CE) effluent was used tc neutralize the reactor effluent, but the CE had to be diluted to five times its original concentration in order not to be inhibitory to the methanogens.

Qiu et al (1987) investigated the anaerobic pretreatment and aerobic post treatment of Kraft evaporator condensate (KEC) and caustic extraction (CE) stage bleaching effluent from a Kraft mill. The anaerobic pretreatment study was conducted with a 3.6 litre USB reactor and the aerobic post treatment with a 2.4 litre activated sludge unit. The results of the study indicated that KEC was easily degraded anaerobically, but that the degradability of CE was limited and that CE was inhibitory to anaerobic organisms.

When only KEC was fed to the anaerobic reactor, COD and BOD_5 removal efficiencies of 70 percent and 90 percent, respectively, were achieved at loading rates below 12.0 kg COD/$m^3 \cdot d$. The COD and BOD_5 removal efficiencies decreased to 32 percent and 52 percent, respectively, as the level of CE inclusion was increased to 50 percent. The specific methane production rate was expected to be 0.29 m^3/kg COD fed for KEC and 0.16 m^3/kg COD fed for CE.

It was suggested that an acclimation period for the micro-organisms would be required to effectively treat a mixture

of KEC and CE. Aerobic post treatment was recommended for further BOD_5 reduction and odour removal.

Cocci et al (1985) evaluated the feasibility of anaerobically treating Kraft foul condensates with a 7 litre bench-scale geotextile media downflow filter anaerobic reactor. A maximum loading rate of 2.1 kg COD/m^3·d was achieved with the addition of yeast extract as a source of micro nutrients. It was suggested that at a loading rate of 10.0 kg COD/m^3·d, COD and BOD_5 removal efficiencies of 80-90 percent could be expected. The average specific methane generation rate observed during the study was 0.29 m^3/kg COD removed.

Pipyn et al (1987) conducted a pilot-scale anaerobic treatability study with a 2 m^3 Polyurethane Carrier Reactor to treat mixed condensates from cooking vessels and block liquor evaporators at a Kraft pulp mill. The wastewater was mainly composed of methanol and had a COD of approximately 12,000 mg/L. After aerobic pretreatment to remove the sulphur compounds, anaerobic reactor loading rates of 12.0-15.0 kg COD/m^3·d were achieved with COD removal efficiencies in the range of 86-88 percent. The incoming wastewater was mixed with recycled effluent for pH control. Phosphate was also added to the incoming wastewater. A feasibility study was conducted to compare the anaerobic treatment of 5,800 kg COD/d from a 400 ton pulp/d plant versus the conventional method of steam stripping followed by aerobic treatment. Anaerobic and conventional aerobic treatment were compared in terms of odour reduction alone and in terms of both odour reduction and COD reduction. In both cases, anaerobic treatment proved to be more economically feasible than aerobic treatment with a net operational benefit of approximately $540,000 for odour reduction alone and approximately $1.5 million for odour and COD reduction.

3.5.3 Other Pulping Processes

Anaerobic treatability studies have also been conducted with waste streams from several other pulping processes. Jurgensen et al (1985) characterized several process effluent streams from the thermo-chemical pulping process to determine the toxicity and biodegradability of the waste streams during anaerobic treatment. The results of the studies showed little toxicity due to any of the waste streams and substantial degradation of the wastewater organics to methane. Anderson et al (1987) conducted laboratory and pilot-scale anaerobic treatability studies with chemi-thermo-mechanical pulping (CTMP) wastewater. The CTMP effluent,

produced from spruce chips which have been impregnated with sodium sulfite before refining, contained 6,000 to 8,000 mg COD/L and 3,000 to 4,000 mg BOD/L. Peroxide toxicity was initially a problem, but was resolved by the addition of a mixture of metal salts. Completely mixed stirred tank reactors were used in the first two stages of the laboratory studies and a one litre USB reactor was used in the third stage. A USB reactor with a total volume of 17 m^3 was used in the pilot-scale study. Organic loading rates of 6.0 kg COD/m^3·d were achieved with the pilot-scale USB reactor and COD and BOD removal efficiencies of 62 percent and 99 percent, respectively, were obtained. The specific methane production rate was 0.25 m^3/kg COD removed. A three-stage process was developed from the data collected during the laboratory and pilot-scale studies and a full-scale plant was designed and constructed. The plant was scheduled to be completed by June 1987.

Wilson et al (1988) evaluated three anaerobic treatment technologies (fluidized bed, upflow anaerobic sludge blanket and anaerobic contact) to treat neutral sulfite semichemical (NSSC) and chemi-thermomechanical pulp (CTMP) effluent at pilot scale. The NSSC and CTMP combined effluent contained 8,800 mg COD/L, 3,700 mg BOD_5/L, 282 mg TSS/L and the pH ranged from 5.8 to 7.1. The USB and anaerobic contact reactors performed well and organic loading rates of 12.0 and 4.0 kg COD/m^3·d, respectively, were achieved. The fluidized bed reactor was shut down after three months because start-up objectives could not be met and acclimation problems were experienced. A USB reactor was eventually selected for a full-scale facility, which was due to be completed by August 1988.

Van Horn et al (1988) conducted a pilot-scale anaerobic treatability study to determine the amenability of primary clarifier effluent from a semi-chemical pulp and paper mill. A one cubic metre low-rate bulk volume fermenter (BVF) was used in the study. The wastewater contained approximately 6,900 to 7,800 mg COD/L, 2,200 to 3,200 mg BOD/L, 400 to 920 mg TSS/L and the pH ranged from 6.8 to 7.1. At an organic loading rate of 1.41 kg COD/m^3·d, COD and BOD removal efficiencies of 41 percent and 85 percent, respectively, were achieved. Budget costs were also developed for a full-scale facility. The system included a BVF with an active volume of 49,100 m^3 and biogas handling equipment. The reactor was designed to be loaded at a rate of 0.56 kg BOD/m^3·d and the BOD removal efficiency was expected to be 85 percent. The capital cost of the full-scale system was

estimated to be in the order of $3 million with annual operating and maintenance costs of $61,000.

Hall et al (1986) evaluated the performance of three anaerobic treatment technologies, anaerobic fluidized bed, upflow anaerobic sludge blanket and upflow anaerobic sludge/fixed film hybrid at pilot-scale to determine the treatability of a combined effluent from an NSSC corrugating mill and hardboard plant. The reactors were initially operated in a single-phase mode, however, higher effluent quality and lower caustic requirements were observed during operation in a two-phase mode. The highest removal efficiencies were achieved with the USB reactor. Approximately 90 percent of the BOD and 56 percent of the COD were removed at an organic loading rate of 14.0 kg COD/$m^3 \cdot d$.

4.0 WASTE STREAMS SELECTION AND CHARACTERIZATION

4.1 Waste Streams Selection

From discussions with organizations involved with the production of fuel grade alcohol, waste streams generated during the various processes were identified and evaluated as to their suitability for energy recovery and waste treatment using anaerobic technology. The waste streams identified were evaluated on the basis of the following considerations:

- Physical and chemical characteristics;
- Potential quantities of waste produced (short- and long-term);
- Energy recovery and utilization potential;
- Current waste treatment, disposal and/or utilization practices for similar waste streams;
- Availability of the waste for laboratory and pilot testing;

Table 4.1 summarizes the individual waste streams identified for the three main Wood-to-Ethanol processes that were investigated.

Figure 4.1 is a simplified block diagram of the unit processes in the Bio-Hol Wood-to-Ethanol process. The main waste streams are indicated. No wastewater characteristics or sample volumes were available for any of these waste streams.

Figure 4.2 is a simplified block diagram of the unit processes for the Iogen Wood-to-Ethanol process. The main waste streams are indicated but during this study no wastewater samples were available for pilot testing.

Figure 4.3 is a simplified block diagram of the unit processes for the Forintek Wood-to-Ethanol process. The main wastewater streams are indicated. A small sample of the lignin recovery wastewater was evaluated during this study.

Table 4.1
POTENTIAL WASTE STREAMS PRODUCED BY THE VARIOUS WOOD-TO-ETHANOL PROCESSES

Bio-Hol	Iogen	Forintek
Hydrolysis Condensate	Steam Explosion Condensate	Steam Explosion Condensate
Hydrolysis Waste	UF Permeate	Lignin Recovery Wastes
Fermentation Residue	Lignin	Evaporator Condensate
Acid-Lignin Waste	Still Condensate	Enzyme Residue
Lignin Fermentation Residue	Still Bottoms	Fermentation Wastes
Lignin		Still Condensate
		Still Bottoms

The Iogen and Forintek processes both use a steam explosion step as a pretreatment of the wood chips prior to hydrolysis and further processing. This pretreatment step results in the production of a steam condensate wastewater of significant volume.

Although Iogen and Forintek were not generating this wastewater, a similar steam explosion pilot plant was being operated at the University of Sherbrooke using the STAKE Technology Ltd.'s Staketech commercial scale continuous steam explosion reactor. Figure 4.4 is a simplified block diagram of the unit process for the Staketech Wood-to-Ethanol process.

This steam explosion pretreatment condensate (SEPC) was selected for initial pilot testing for the following reasons:

- Common waste stream to most Canadian Wood-to-Ethanol processes;
- Large volume of wastewater generated in the process;

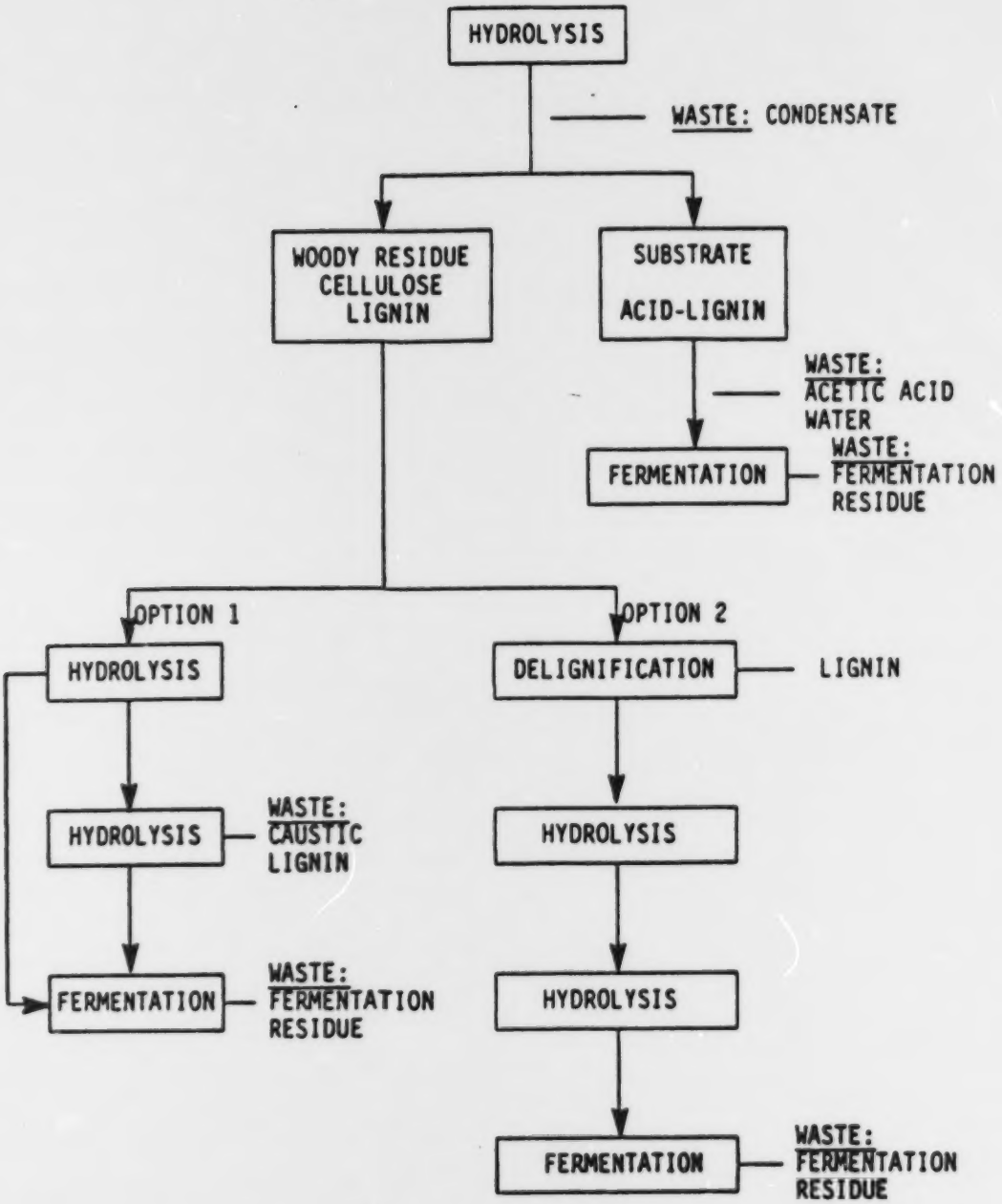


Figure 4.1

Waste Streams Generated from the Bio-Hol Developments Wood-to-Ethanol Process

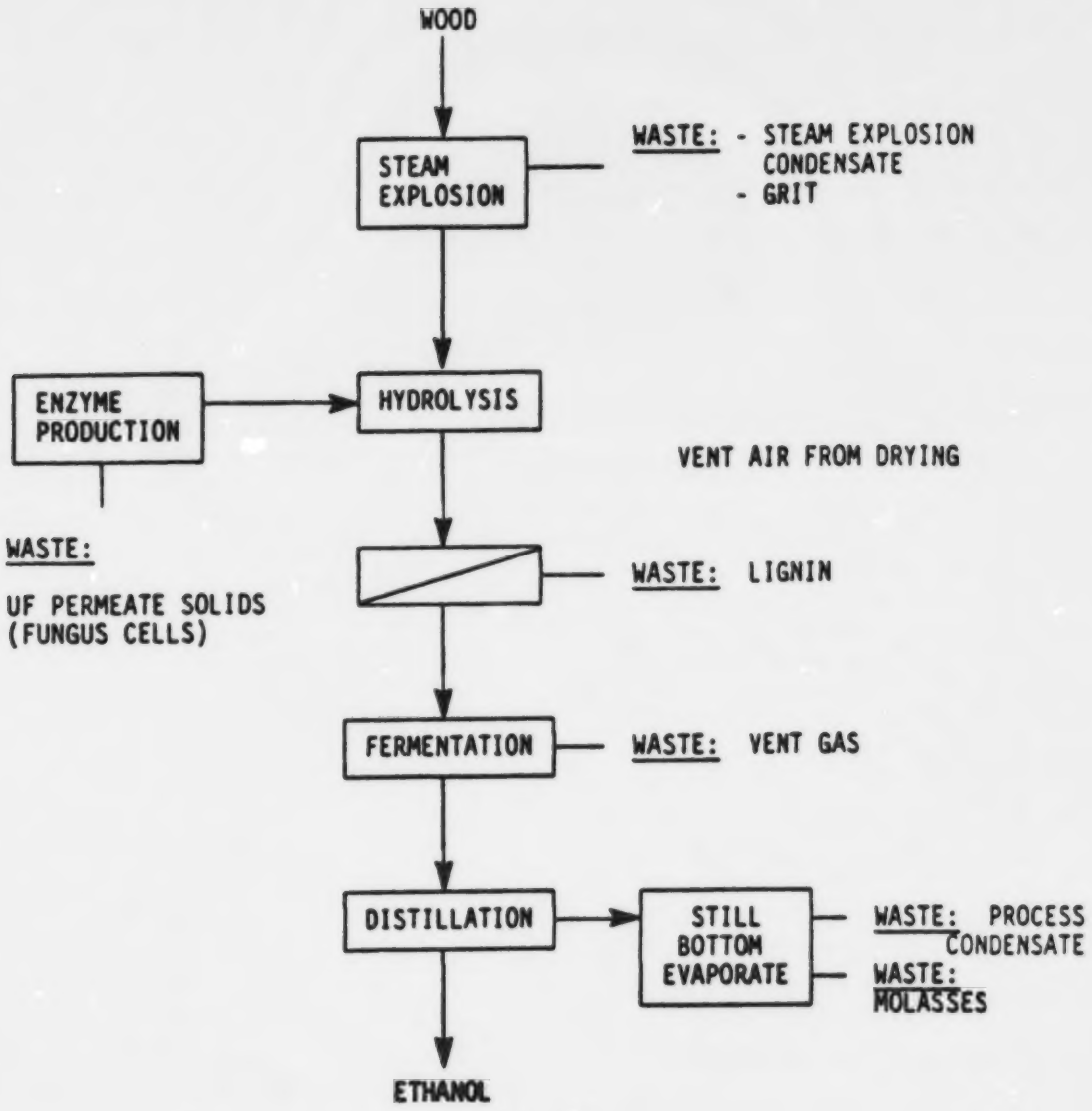


Figure 4.2
Waste Streams Generated from the Iogen Wood-to-Ethanol Process

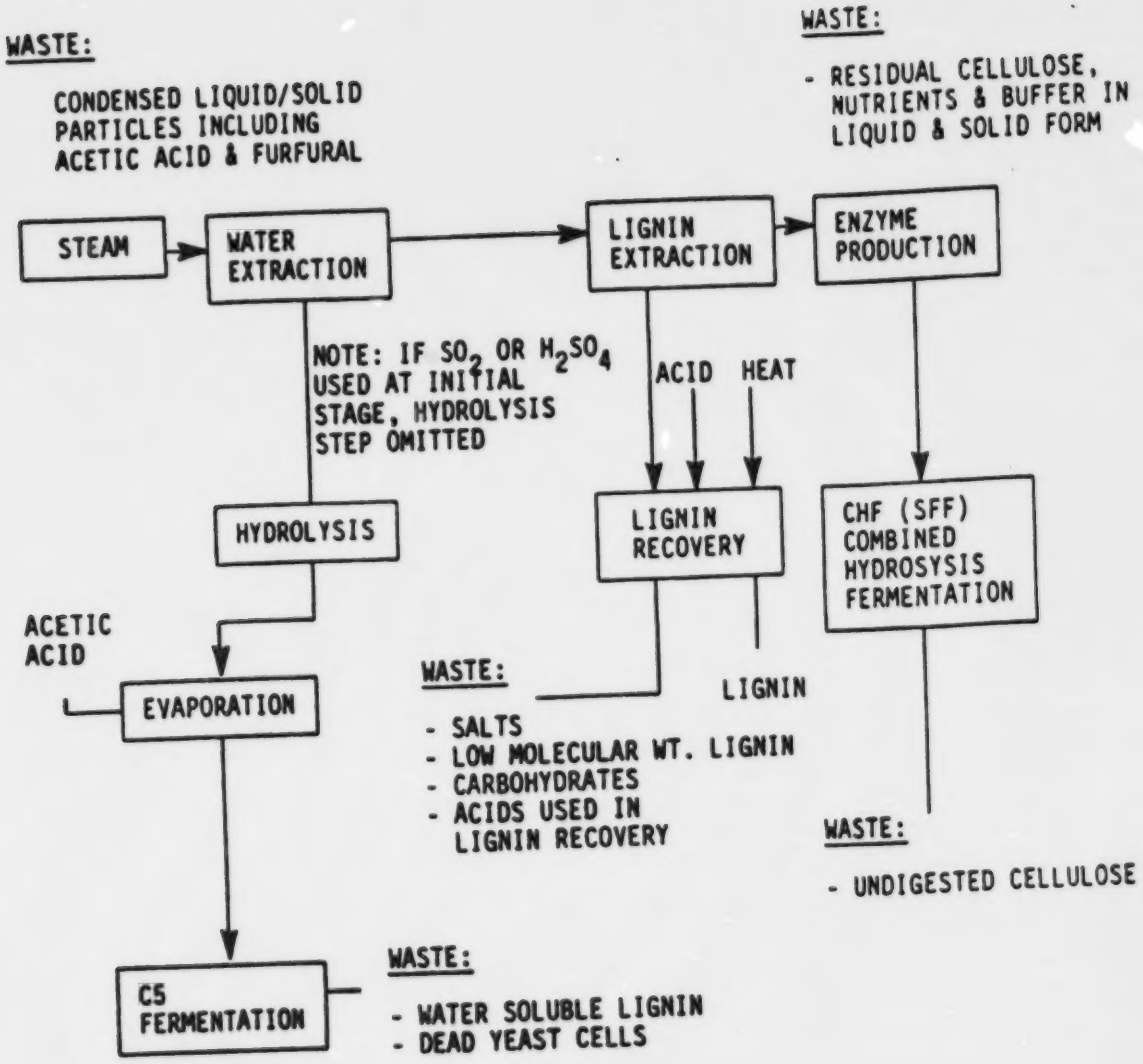


Figure 4.3
Waste Streams Generated from the Forintek Wood-to-Ethanol Process

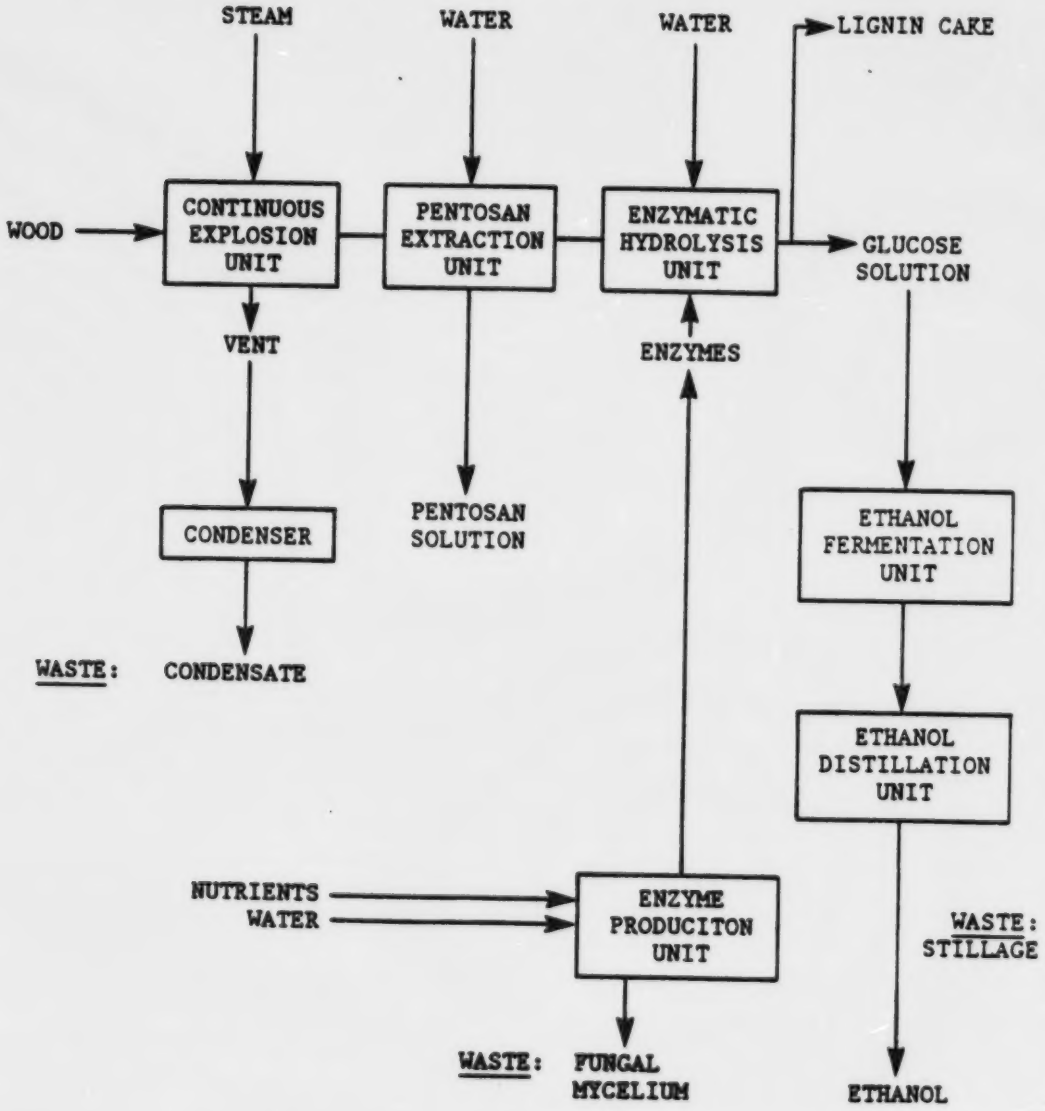


Figure 4.4
Waste Streams Generated from the Staketech Continuous Wood-to-Ethanol Process

- Waste stream was currently available in sufficient quantities to run pilot studies;
- Lack of treatability data on this waste stream;

A second waste stream from the lignin recovery operation was evaluated for possible anaerobic toxicity effects by using a standard anaerobic toxicity assay (ATA) testing procedure.

The lignin recovery waste stream was produced through steam explosion followed by solvent/alkaline extraction process.

4.2 Waste Streams Characterization

A complete waste stream characterization was conducted at the outset of the treatability studies to determine the physical and chemical characteristics of the SEPC waste and the lignin recovery waste. The results are presented in Tables 4.2 and 4.3, respectively.

The type of wood and operating conditions are summarized in the table for each of the runs performed on the STAKE Pilot plant. All of these SEPC samples were used to feed the anaerobic reactors. The lignin recovery wastewater was sampled during the lignin recovery experiments performed at Forintek.

As shown in Table 4.3, the SEPC wastewater characteristics varied considerably. Waste characteristics were dependent on the production process operating conditions (time, pressure, and temperature). The chemical oxygen demand (COD) of the condensate ranged from 3,000 to approximately 20,000 mg/L. Furfural concentrations ranged from 60 to 5,100 mg/L. The strongest waste was generated at 391 psi pressure, 230°C temperature, and at 2 minutes operating time.

The lignin recovery waste (Table 4.3) was relatively weak in comparison (4,500 mg COD/L), but because of the high dissolved solids may have been potentially inhibitory to methanogenic bacteria.

Table 4.2
CHARACTERISTICS OF SEPC SAMPLES PRODUCED
UNDER VARYING OPERATING CONDITIONS

Sample	Operating Conditions	pH	TS (mg/L)	TVS (mg/L)	COD (mg/L)	TP (mg/L)	TKN (mg/L)	Methanol (mg/mL)	Furfural (mg/mL)	Acetic Acid (mg/mL)
1) Hardwood										
Batch 1	2 min, 220°C, 2240 kpa (325 psi)	3	575	96	21,290	<1	0.9	2.3	4.8	8.5
Batch 2										
Run 1	2 min, 190°C, 1151 kpa (167 psi)		25	100	3,090	0.07	1.33	1.4	0.06	0.06
Run 2	2 min, 230°C, 2696 kpa (391 psi)		720	97.3	20,360	0.12	1.27	1.9	5.1	7.0
Batch 3										
Run 1	2 min, 190°C, 1151 kpa (167 psi)	2.5	135	100	4,500	0.14	0.58	1.0	0.6	1.4
Run 2	2 min, 219°C, 2220 kpa (322 psi)	2.5	550	100	19,460	<0.07	1.15	2.1	4.9	6.6
Run 3	2 min, 229°C, 2696 kpa (391 psi)	2.5	500	100	15,860	0.17	1.18	1.0	2.9	5.1
2) Softwood										
Batch 1										
Run 1	2 min, 200°C, 1462 kpa (212 psi)	2.8	360	350	8,990	<0.2	<1.0	1.9	2.4	1.9
Run 2	2 min, 210°C, 1806 kpa (262 psi)	2.3	1,905	1,335	10,700	<0.2	<1.0	1.7	1.4	1.4
Run 3	2 min, 224°C, 2413 kpa (350 psi)	2.2	2,125	1,535	9,210	<0.2	<1.0	2.2	1.2	1.6

Table 4.3
LIGNIN RECOVERY WASTE CHARACTERIZATION DATA

Parameter	Concentration*
pH	1.8
COD (total)	4,490
COD (soluble)	4,200
BOD	1,480
TS	16,360
TVS	7,080
TDS	13,660
VDS	5,465
TP	4.64
NH_3-N	5.6
TKN	4.8**
Phenol	77.2
Metals	
Aluminum	4.57
Barium	0.21
Beryllium	< 0.005
Boron	<0.01
Cadmium	<0.012
Calcium	29.2
Chromium	0.18
Cobalt	<0.03
Copper	0.25
Iron	24.8
Lead	0.34
Magnesium	2.29
Manganese	0.14
Nickel	<0.02
Phosphorus	0.14
Silver	<0.02
Sodium	3,130
Strontium	<0.04
Vanadium	<0.01
Zinc	0.30

* All concentrations in mg/L except for phenol (in µg/L) and pH.
** Interferences detected.

5.0 EQUIPMENT AND METHODS

5.1 SEPC Waste Stream Continuous Flow Testing

Three anaerobic flow-through reactors were used. A simplified schematic of the pilot plants is shown in Figure 5.1. Two reactors (R_1, R_2: 16.9 L active volume each) were upflow sludge blanket (USB), and one (R_3: 13.7 L active volume) was a downflow fixed film (FF) reactor. All of the pilot plants consisted of a raw waste feed tank and variable flow feed pump, a recycle pump, a reactor and a biogas handling train including a sampling port and gas flow meter.

A pre-acidification tank with a retention time of approximately 4 hours was placed upstream of reactors 1 and 2 to evaluate the effect of pre-hydrolysis on USB performance after about 3 months of operation. The fixed film reactor was operated in a downflow mode during the entire study.

The fixed film reactor was seeded with municipal anaerobic digester sludge and the two USB reactors were seeded with granulating sludge from a pilot plant operating on pulp and paper wastes. All reactors were operated at 35°C (mesophilic temperature range).

Photograph 5.1 shows the set-up of the three continuous flow reactors. Photograph 5.2 shows the plastic media used in the fixed film reactor both in its unused state, and with the attached growth.

Table 5.1 is a list of the major operational events in the treatability study of the SEPC. At the initialization of the project no wastes from any of the Wood-to-Ethanol processes were available in sufficient quantity for pilot testing. In order to develop some attached growth on the fixed film media and to stabilize and develop some granular sludge in the USB reactors, all three reactors were started up on April 4, 1988 and operated on a combination of municipal digester supernatant and cheese whey until early May 1988 when they were fed a 1:10 dilution of the steam explosion pretreatment condensate (SEPC). The SEPC was diluted because the characterization data had shown that the level of furfural contained in the condensate is approximately ten times higher than the toxic levels reported in the literature for unacclimated anaerobic microorganisms. The rate of dilution was decreased as the anaerobic microorganisms

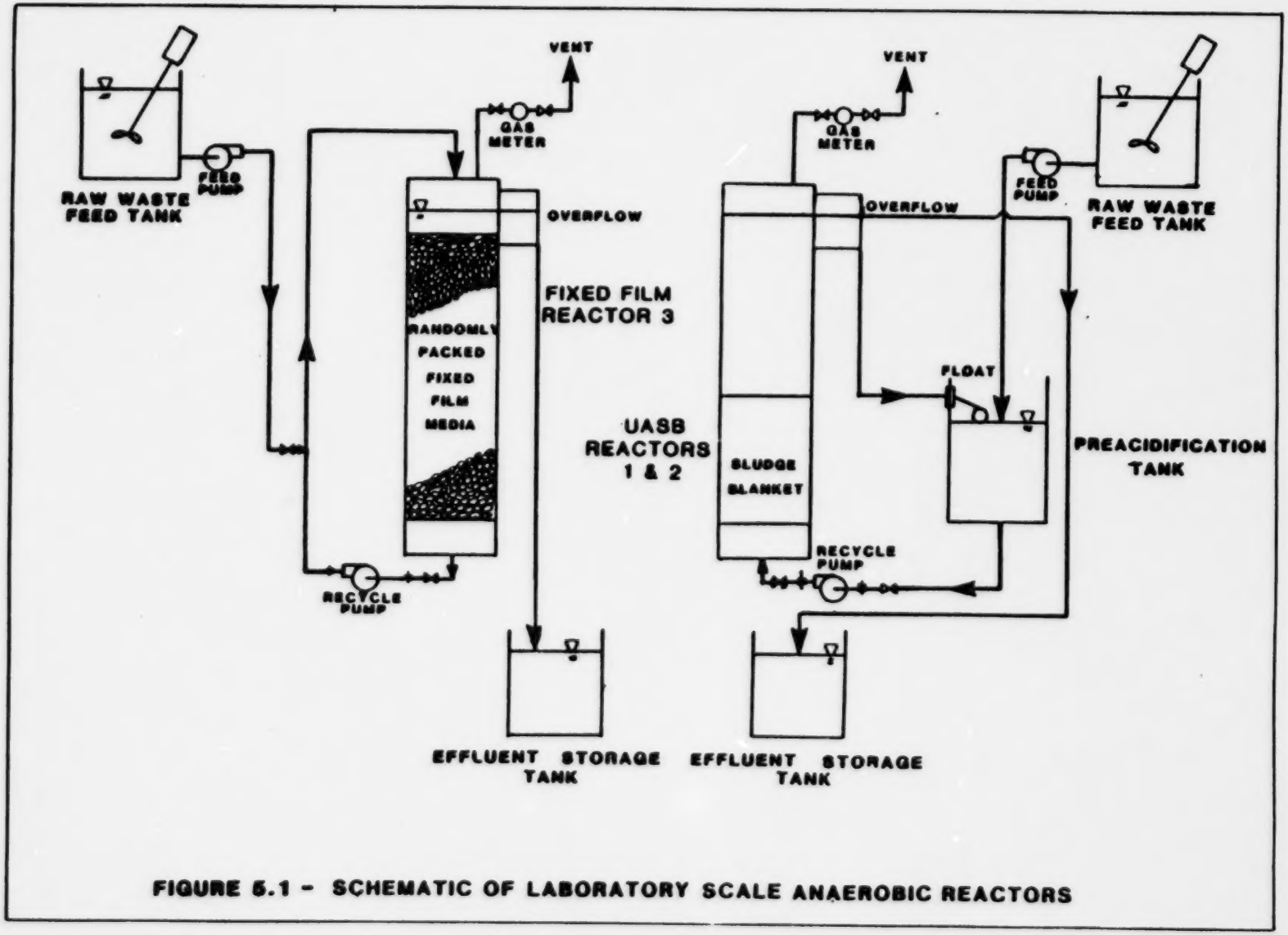
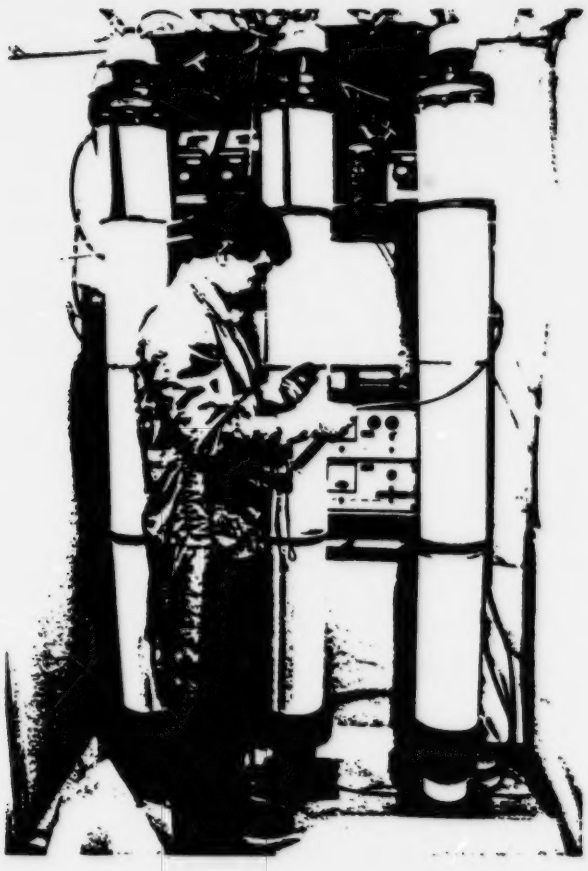


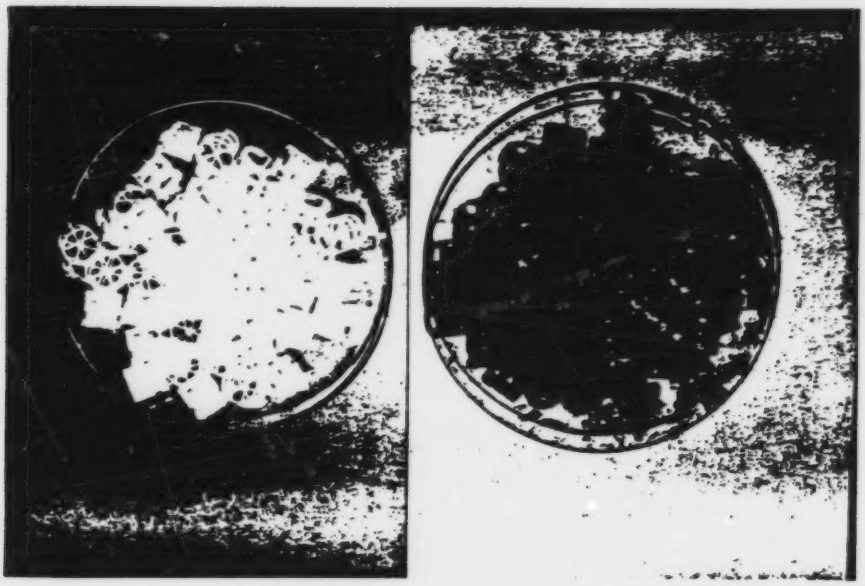
FIGURE 5.1 - SCHEMATIC OF LABORATORY SCALE ANAEROBIC REACTORS



Photograph 5.1
SET-UP OF CONTINUOUS FLOW REACTORS

Table 5.1
LIST OF THE MAJOR OPERATIONAL EVENTS AND PROBLEMS DURING TREATABILITY TESTING OF SEPC

Day (Date)	Reactor 1 (USB)	Reactor 2 (USB)	Reactor 3 (FF)	Activated Sludge
April 4, 1988	Start-up	Start-up	Start-up	
Day 1 (June 1, 1988)	Stabilized operation, first day of SEPC addition	Stabilized operation, first day of SEPC addition	Stabilized operation, first day of SEPC addition	
Day 34 (July 4, 1988)	First day of nutrient addition	First day of nutrient addition	First day of nutrient addition	
Day 56 (July 26, 1988)	Full strength waste fed by mistake (COD = 20,000 mg/L)	Full strength waste fed by mistake (COD = 20,000 mg/L)	Full strength waste fed by mistake (COD = 20,000 mg/L)	
Day 78 (August 17, 1988)			Thermostat mal function (temp erature = 40°C)	
Day 85 (August 24, 1988)	PAT installed			
Day 86 (August 25, 1988)		PAT installed		
Day 118 (September 26, 1988)				Start-up
Day 126 (October 4, 1988)		PAT removed	No heat in trailer	
Day 136 (October 14, 1988)			Heat tracer malfunction (temperature = 39°C)	
Day 148 (October 26 , 1988)	First day of no NaOH addition	First day of no NaOH addition	First day of no NaOH addition	
Day 160 (November 7, 1988)	Shut down			
Day 164 (November 11, 1988)		Furfural addition		
Day 171 (November 18, 1988)			Furfural addition	
Day 192 (December 9, 1988)		Shut down	Shut down	Shut down



Photograph 5.2
PLASTIC MEDIA USED IN THE FIXED FILM REACTOR
(BEFORE AND AFTER THE TREATABILITY TESTING)

became acclimated to the presumably toxic compounds contained in the condensate. June 1, 1988 was considered to be the first day of stabilized operation.

The initial characterization of the SEPC indicated a deficiency in some essential nutrients and minerals such as N, P, Fe, Mo, Co, Ni and sulphur.

A nutrient and mineral mixture was prepared and was added to the anaerobic reactors' feed starting on day 34. Table 5.2 summarizes the nutrient and the mineral mix used during the study.

A 10 mL aliquot of the nutrient and mineral mixture was added to each litre of full strength SEPC before dilution and feeding to the reactor. This resulted in target nutrient and mineral concentrations in the SEPC as follows;
N: 650 mg/L, P: 65 mg/L, Fe: 40 mg/L, Mo: 1.2 mg/L,
Co:1.0 mg/L, Ni: 1.0 mg/L, S: 25 mg/L.

Table 5.2
THE NUTRIENT AND MINERAL MIX
USED FOR THE FLOW-THROUGH REACTORS

Chemical	Formula	Concentration in the Stock Solution (g/L)
Urea	NH_2CONH_2	139.3
Phosphorus pentaoxide	P_2O_5	14.9
Ferric chloride hexahydrate	$FeCl_3 \cdot 6H_2O$	19.3
Ammonium molybdate tetrahydrate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.22
Cobalt chloride hexahydrate	$CoCl_2 \cdot 6H_2O$	0.4
Nickel chloride hexahydrate	$NiCl_2 \cdot 6H_2O$	0.4
Potassium sulfate	K_2SO_4	13.6

Performance of the anaerobic reactors was monitored for approximately 6 months. The performance monitoring schedule followed in this study is summarized in Table 5.3. Whenever steady operating conditions for one of the three reactors was achieved (as signalled by consistently low effluent COD concentrations and low reactor VA/BA ratios, steady biogas production, and optimum effluent pH values), the organic loading rate for the reactor was increased. In most cases, performance of the anaerobic reactors improved with time after every increase in loading.

Table 5.3
PERFORMANCE MONITORING SCHEDULE FOR THE SEPC
TREATABILITY STUDIES (FLOW-THROUGH REACTORS)

Parameter/Analysis	Influent	Effluent	Biogas
Volume	daily	daily	daily
Temperature	daily	daily	-
pH	daily	daily	-
TS	2/week	2/week	-
TVS	3/week	2/week	-
Total volatile acids	3/week	2/week	-
Bicarbonate alkalinity	3/week	2/week	-
COD	3/week	2/week	-
BOD5	1/month	1/month	-
Biogas analysis	-	-	1/week
Metals scan	Periodically	Periodically	-

Reactors 1 (on day 86) and 2 (on day 85) were modified to include a pre-acidification stage. This was done to evaluate the effect of separating the hydrolysis/acidification stages from the methanogenic stage. The pre-acidification tanks (PATs) also acted as equalization tanks prior to the anaerobic reactors.

In order to investigate the effect of higher furfural concentrations on the performance of the anaerobic units, the SEPC feed for reactors 2 (on day 164) and 3 (on day 171) was spiked with higher levels of furfural during the last 6 weeks of operation.

To assess the potential for further anaerobic effluent polishing as might be required if the treated effluent were disposed of in a surface body of water (stream or lake), a pilot-scale activated sludge system (10 litres volume) was constructed and went into operation on day 118. A schematic of the activated sludge system is shown in Figure 5.2 (also see Photograph 5.3). The activated sludge system was operated in the high-rate mode (target F/M = 1.5 d^{-1}, MLVSS = 4,000 mg/L, HRT = 0.5d, and SRT = 5d).

5.2 Lignin Recovery Waste Stream ATA Testing

An anaerobic toxicity assay (ATA) test was set up to investigate the possible inhibitory effects of the lignin recovery wastewaters on anaerobic microorganisms. The method used by Cornacchio et al (1986) [a modification of the serum bottle bioassay techniques described by Owen et al (1979)] was followed.

The ATA test was performed using 125 mL Erlenmeyer flasks which were placed in a water bath inside an incubator which was maintained at 35°C. Varying concentrations of the wastewater, a nutrient supplement, and sludge obtained from a municipal digester were transferred into the ATA units that were kept oxygen-free during dispensing by continuous gassing with a 30% CO_2/70% N_2 mixture. All flasks were spiked with an aliquot of volatile organic acids.

The nutrient supplement (or growth medium) was prepared by combining the stock solutions as outlined in Table 5.4 (page 5-11) in the proportions given in Table 5.5 and boiling for 3 minutes, and adding 3.4 g of $NaHCo_3$ as a buffer. The medium was cooled and brought to a 1 litre volume with distilled water.

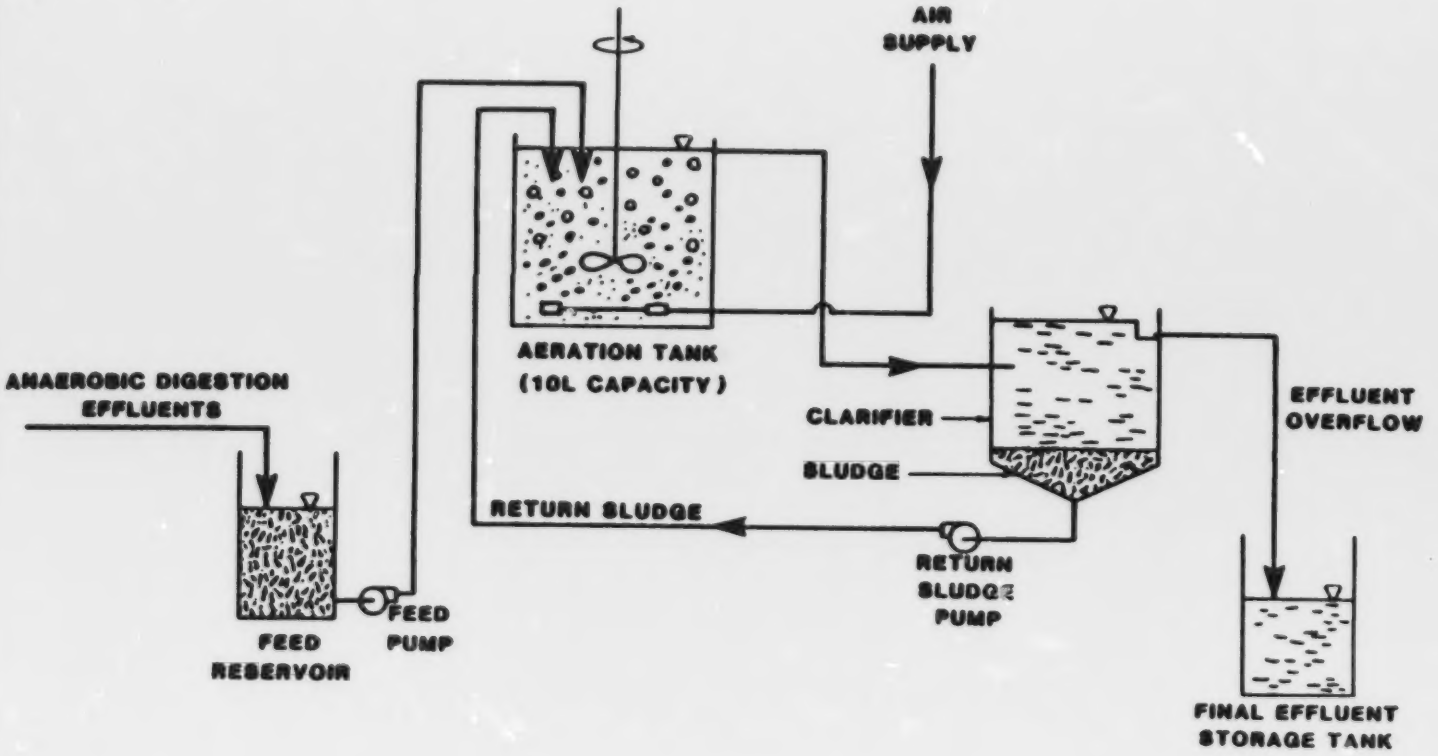
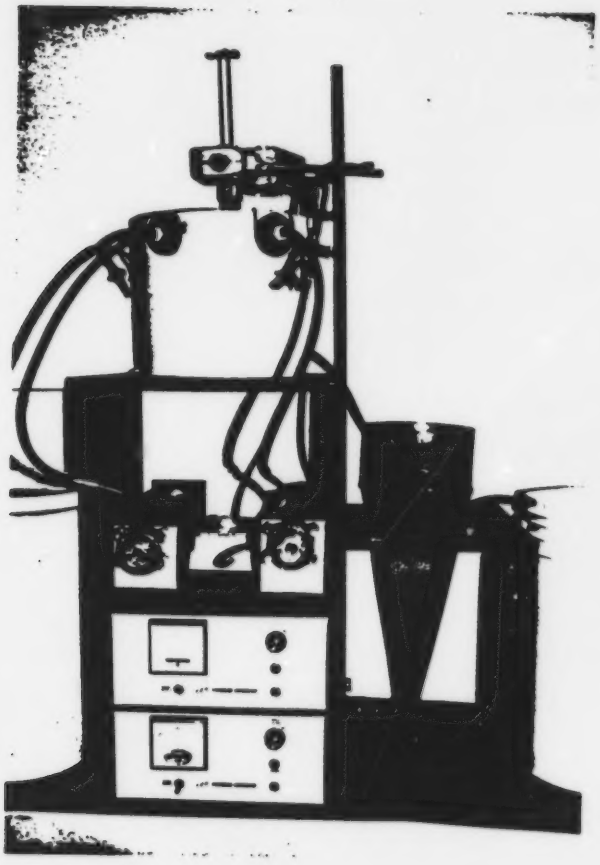


FIGURE 5.2 - SCHEMATIC OF BENCH-SCALE ACTIVATED SLUDGE EFFLUENT POLISHING SYSTEM



Photograph 5.3
SET-UP OF THE ACTIVATED SLUDGE POLISHING SYSTEM

The contents of the ATA flasks were mixed manually once a day to accelerate the mass transfer rate and assist in the substrate-microorganism contact.

The generated gas was collected in 60 mL graduated syringes. The gas volume was monitored daily and was recorded whenever additional gas production was observed. Photograph 5.4 shows the assay set-up.

In conjunction with the ATAs, a set of spiked controls were run. The inhibitory effect of the wastewater was determined by comparing the differences in methane production rates in the test units with those in the spiked blanks.

5.3 Analytical Procedures

All analytical tests were performed according to the sixteenth edition of "Standard Methods for the Examination of Water and Wastewater" (APHA/AWWA/WPCF/1985) published by the American Public Health Association (APHA), American Water Works Association (AWWA) and the Water Pollution Control Federation (WPCF). Gas analysis was performed on a Fisher Model 25 Gas Partitioner using a Poropak P column equipped with a Thermal Conductivity detector.

The volatile acids were monitored using the titration method originally introduced by DiLallo and Albertson (1961). Metals scan were done by ICAP methods on acid digested samples.

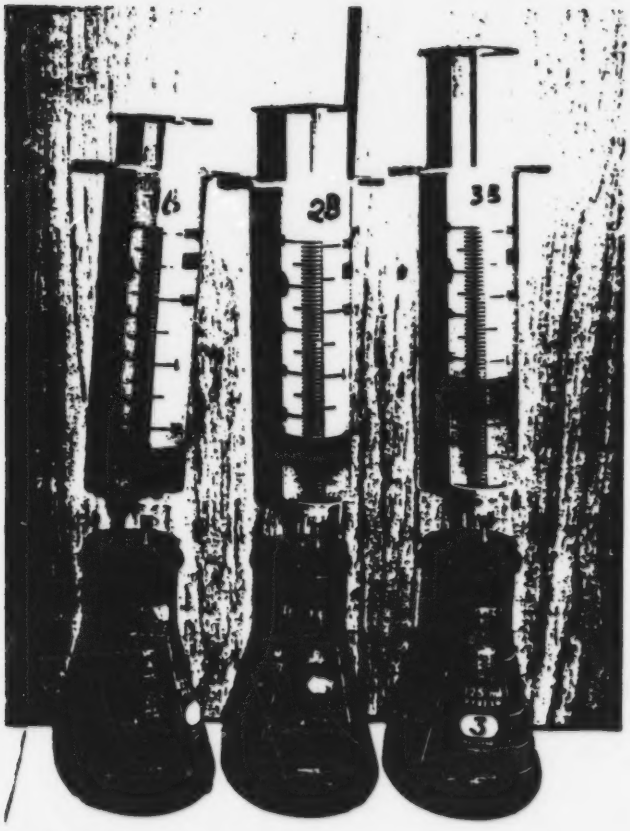
Table 5.4
STOCK SOLUTIONS USED IN THE GROWTH MEDIUM

Solution	Components	Concentration in Distilled Water (g/L)
Mineral I[1]	NaCl	50
	$CaCl_2 \cdot 2H_2O$	10
	NH_4Cl	189.4
	$MgCl_2 \cdot 6H_2O$	10
Mineral II	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	10
	$ZnSO_4 \cdot 7H_2O$	0.1
	H_3BO_3	0.3
	$FeCl_2 \cdot 4H_2O$	1.5
	$CoCl_2 \cdot 6H_2O$	10
	$MnCl_2 \cdot 4H_2O$	0.03
	$NiCl_2 \cdot 6H_2O$	0.03
	$AlK(SO_4)_2 \cdot 12H_2O$	0.1
Vitamin B	Nicotinic acid	0.1
	Cyanocobalamine	0.1
	Thiamine	0.05
	p-aminobenzoic acid	0.05
	Pyridoxine	0.25
	Pantothenic acid	0.025
Phosphate	KH_2PO_4	50
Resazurin		0.1
2-methyl-n-butyric acid[2]		102
Sulphide[3]	$Na_2S \cdot 9H_2O$	25

(1) Dissolved in 0.01 M HCl rather than distilled water.
(2) Adjusted to pH 6.5.
(3) Prepared in small aliquots in freshly boiled water just prior to use.

Table 5.5
COMPOSITION OF THE GROWTH MEDIUM VOLUME

Solution	(ml)
Distilled water	900
Mineral I	10
Mineral II	1
Vitamin B	1
Phosphate	10
Resazurin	15
2-methyl-n-butyric acid	1



Photograph 5.4
SET-UP OF THE ATA TESTING APPARATUS

6.0 RESULTS AND DISCUSSION

6.1 SEPC Treatability Testing

6.1.1 Performance of the Continuous Flow Reactors

Results of the performance monitoring tests were plotted against time. Figures 6.1 and 6.2 illustrate typical plots of chemical oxygen demand (COD) and biogas production, respectively for each anaerobic reactor. In addition to influent and effluent COD, and biogas production, other parameters such as influent and effluent pH, reactor total alkalinity, bicarbonate alkalinity, and volatile acids/bicarbonate alkalinity (VA/BA) ratio were analyzed.

From Figures 6.1 and 6.2, it is evident that increases in the influent COD concentrations and loadings were generally followed by a net increase in biogas production. It was noted that initially biogas production rates decreased and reactor performance deteriorated after every large increase in organic loading. In most cases, however, performance of the anaerobic reactors improved with time resulting in a stable operation at progressively higher loading rates.

For example, the COD removal efficiency of Reactor 2 (USB system) dropped from 56% (on day 65) to 24% (on day 66) when the COD loading was increased from 3.2 to 4.2 kg/m^3·d. However, after operating the system at the 4.2 kg COD/m^3·d loading rate, the COD removal efficiency returned (in actual fact improved) to 83% on day 73.

In addition to the scheduled load increases, unexpected operational problems also showed detrimental effects on the performance of the anaerobic reactors. For example, the thermostat malfunction on day 78 (see Table 5.1) resulted in a deterioration of Reactor 3 (fixed film) performance on day 79. The COD removal efficiency dropped from 92% prior to the malfunction to 28% after the malfunction. Very low biogas production volumes shown in Figure 6.2 were likely due to the meter inaccuracy rather than an indication of a poor reactor performance.

In the later stages of the treatability testing, organic loading to the anaerobic reactors was increased at considerably faster rates, without a significant drop in performance. This is an indication of a progressive acclimation of the anaerobic microorganisms to SEPC. For example,

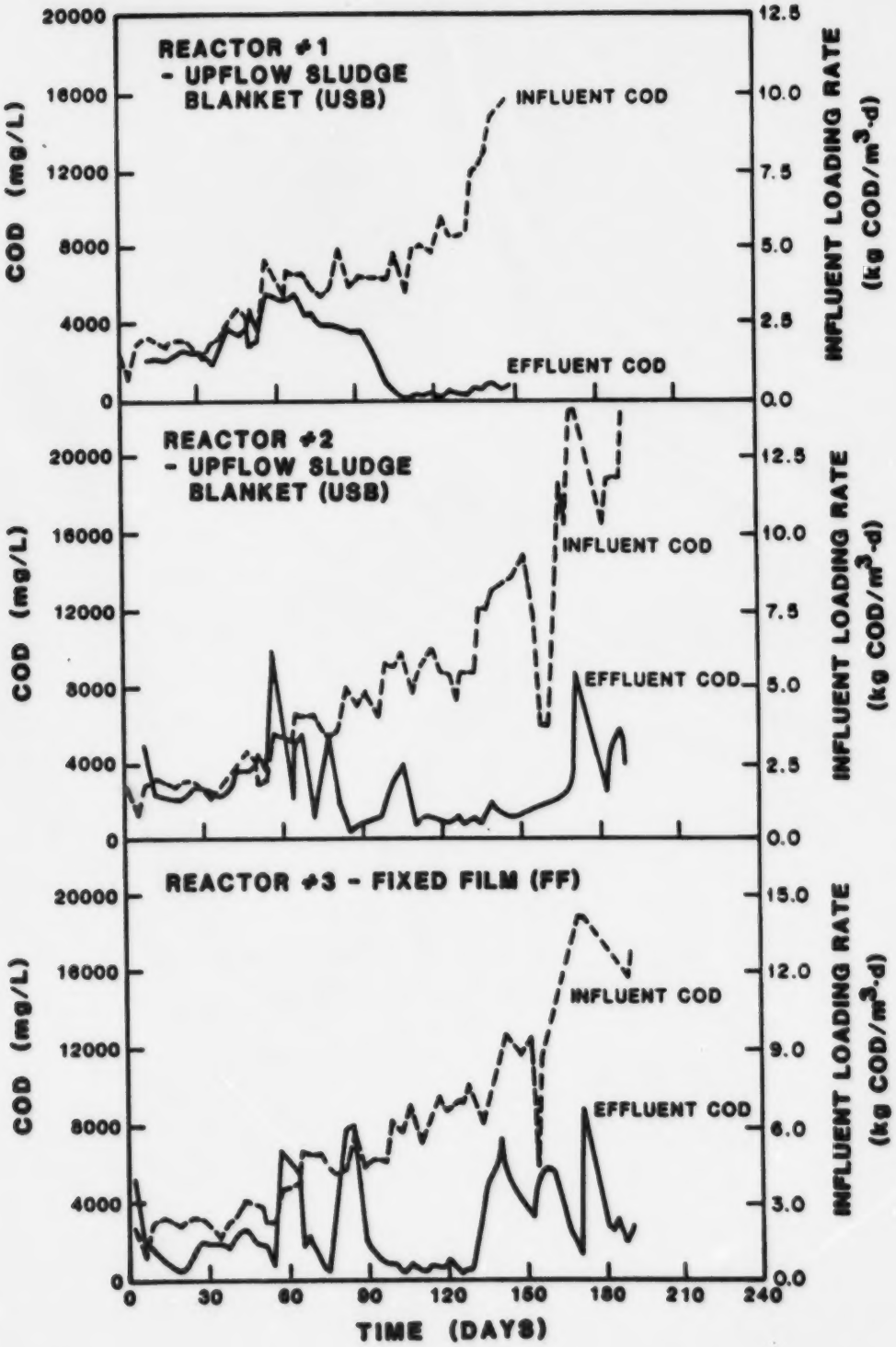


FIGURE 6.1: SUMMARY OF PERFORMANCE OF FLOW-THROUGH REACTORS IN TERMS OF CHEMICAL OXYGEN DEMAND (COD)

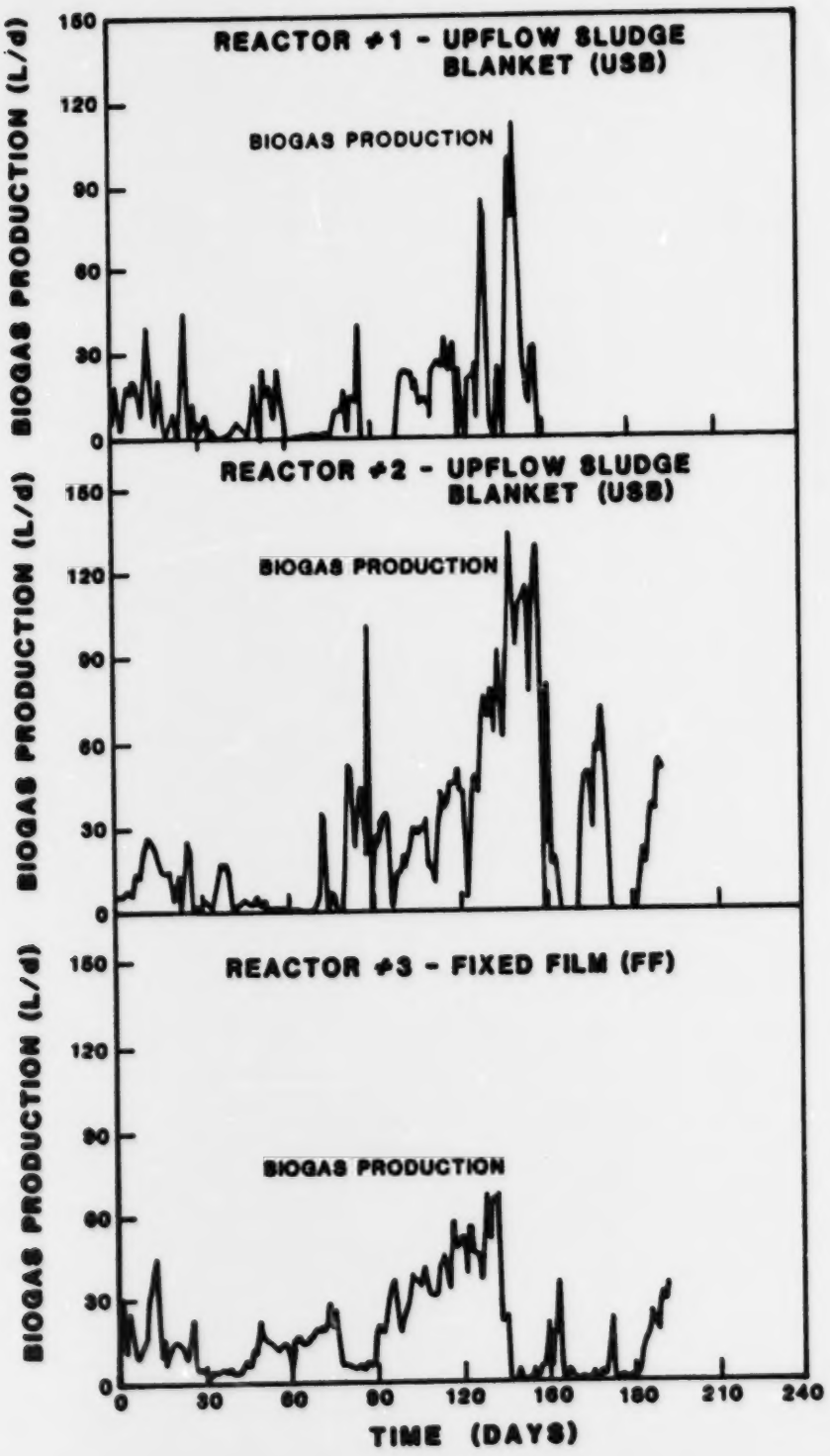


FIGURE 6.2: SUMMARY OF PERFORMANCE OF FLOW-THROUGH REACTORS IN TERMS OF BIOGAS PRODUCION

increase of Reactor 2 (USB system) COD load from 5.4 (on day 134) to 7.5 (on day 136) resulted in the improved performance of the system, as the COD removal increased from 86% to 93%, respectively. The biogas production also improved from 65 litres/d before to 89 litres/d after the load increase.

In an attempt to quantify the reactors' performance trends and using the performance plots such as those shown in Figures 6.1 and 6.2, the entire treatability period was divided into shorter monitoring periods for each reactor. The selected periods were generally representative of the stabilized (quasi-steady-state) conditions achieved after every load increase. Tables 6.1 to 6.3 list the typical information that was compiled for each monitoring period. The averaged results are given for each parameter.

As shown in Tables 6.1, 6.2 and 6.3, the HRT of Reactors 1 and 2 (USB systems) was maintained at 1.6 days. The HRT of Reactor 3 (fixed film system) was kept at 1.3 days for the entire treatability study.

Table 6.1 shows increasing average COD removal efficiencies for Reactor 1 with increased influent COD concentrations and loading rates from period 1 to 5. From period 1 to 5, the COD removal efficiency increased from 21% at 2 kg COD/$m^3 \cdot d$ to 95% at 8.6 kg COD/$m^3 \cdot d$ loading rate.

Total volatile acids (TVA) and the VA/BA ratio increased initially from period 1 to period 2 with increasing COD loadings. Both parameters, however, dropped drastically from TVA=2373 mg/L and VA/BA=7.6 in period 2 to TVA=99 mg/L and VA/BA=0.04 in period 4. The decrease in TVA resulted in increased biogas production.

Specific biogas production for R_1 also increased from 0.05 to 0.32 LCH_4/g COD (removed) with increasing loads from period 1 to 5. Biogas production increased from 6 to 64 litres and its methane content increased from 5% to 69% for the same time period.

Performance of Reactors 2 and 3 followed a similar pattern to the performance of Reactor 1 (see Tables 6.2 and 6.3). In the period (period 1 to 3) before the furfural addition, the COD reduction achieved by R_2 increased from 17% to 89% when the loading rate was increased from 2.1 to 6.5 kg/$m^3 \cdot d$. The performance improved from 48% to 92% when the R_3 COD loading rate was increased from 2.4 to 6.6 (period 1 to 3).

Table 6.1
PERFORMANCE MONITORING PERIODS FOR USB REACTOR, R_1

Reactor 1 (USB)	Period 1 (Day 14-49)	Period 2 (Day 50-82)	Period 3 (Day 83-112)	Period 4 (Day 113-135)	Period 5 (Day 136-149)
Temperature (^oC)	35	35	35	34	34
HRT (days)	1.6	1.6	1.6	1.6	1.6
Dilution Factor (%)	13	38	31	49	78
$COD_{influent}$ (g/L)	3.2 (0.66) n=10	5.2 (1.3) n=10	6.4 (0.77) n=9	8.4 (0.59) n=7	13.8 (1.4) n=6
COD Loading Rate (g COD/L/d)	2.0 (0.43) n=9	3.3 (0.81) n=10	4.0 (0.48) n=9	5.2 (0.35) n=7	8.6 (0.88) n=6
$pH_{(effl)}$	6.4 (0.49) n=31	6.8 (0.44) n=31	7.5 (0.57) n=24	7.8 (0.29) n=23	7.5 (0.15) n=14
COD reduction (%)	21 (9.2) n=9	22 (7.4) n=6	65 (24.7) n=8	96 (1.18) n=7	95 (1.05) n=6
Total Volatile Acids (mg/L)	997 (160) n=8	2373 (802) n=13	1402 (1037) n=12	99 (102) n=9	183 (130) n=5
Total Alkalinity (mg/L)	885 (181) n=8	2055 (637) n=13	2593 (206) n=12	2526 (169) n=9	2567 (229) n=5
VA/BA Ratio n=5	5.8 (1.66) n=8	7.6 (4.26) n=13	1.9 (2.07) n=12	0.04 (0.05) n=9	0.08 (0.07)
*Specific Biogas Production (LCH_4/gCOD added)	0.01	0.03	0.11	0.20	0.30
*Specific Biogas Production (LCH_4/gCOD removed)	0.05	0.15	0.17	0.21	0.32
Methane content (% of volume)	5.1 (4.3) n=3	30.5 (22.2) n=3	69.8 (10.7) n=9	69.8 (9.6) n=4	69.2 n=1
Biogas Production (L/d) n=14	6.4 (9.2) n=25	5.8 (7.4) n=33	10.9 (10.6) n=30	25.6 (22.3) n=23	63.7 (68.3)

* Calculated parameter
n = number of samples
( ) = standard deviation

Table 6.2
PERFORMANCE MONITORING PERIODS FOR USB REACTOR, R_2

Reactor 2 (USB)	Period 1 (Day 13-56)	Period 2 (Day 57-113)	Period 3 (Day 114-163)	Period 4 (Day 164-179)	Period 5 (Day 180-192)
Temperature (°C)	35	35	35	35	35
HRT (days)	1.6	1.6	1.6	1.6	1.6
Dilution Factor (%)	23	35	62	98	84
$COD_{influent}$ (g/L)	3.2 (0.62) n=14	7.0 (1.4) n=16	10.5 (2.8) n=17	20.0 (2.6) n=4	15.6 (7.2) n=5
COD Loading Rate (g COD/L/d)	2.1 (0.40) n=13	4.4 (0.86) n=16	6.5 (1.69) n=17	7.7 (1.18) n=4	3.9 (1.74) n=5
$pH_{(effl)}$	6.5 (0.52) n=38	7.5 (0.42) n=48	7.2 (0.65) n=50	6.7 (0.64) n=15	7.3 (0.56) n=13
COD reduction (%)	17 (9.5) n=11	68 (23.8) n=13	89 (2.9) n=13	85 (2.22) n=3	78 (4.93) n=4
Total Volatile Acids (mg/L)	951 (240) n=12	1444 (980) n=22	592 (537) n=20	2635 (1497) n=8	2169 (742) n=5
Total Alkalinity (mg/L)	887 (234) n=12	2791 (556) n=22	2618 (628) n=20	3166 (319) n=8	3483 (654) n=5
VA/BA Ratio	7.1 (5.6) n=12	2.5 (2.8) n=22	0.23 (0.14) n=19	16.6 (24.5) n=8	1.2 (0.56) n=5
* Specific Biogas Production (LCH_4/gCOD added)	0.01	0.13	0.27	0.07	-
* Specific Biogas Production (LCH_4/gCOD removed)	0.03	0.19	0.31	0.08	-
Methane content (% of volume)	2.4 (1.1) n=4	50.6 (30.5) n=11	53.2 (11.1) n=7	50.5 n=1	-
Influent Furfural Concentration (g/L)	-	-	-	4.5 (3.7) n=15	6 (2.97) n=12
Biogas Production (L/d) n=12	7.4 (7.4) n=38	18.4 (19.0) n=57	56.8 (40.8) n=50	27.9 (27.9) n=16	28.6 (19.1)

* Calculated parameter
n = number of samples
( ) = standard deviation

Table 6.3
PERFORMANCE MONITORING PERIODS FOR FF REACTOR, R_3

Reactor 3 (FF)	Period 1 (Day 8-53)	Period 2 (Day 54-98)	Period 3 (Day 99-130)	Period 4 (Day 131-170)	Period 5 (Day 171-180)	Period 6 (Day 181-192)
Temperature (^oC)	35	35	35	35	35	35
HRT (days)	1.3	1.3	1.3	1.3	1.3	1.3
Dilution Factor (%)	16	31	48	47	63	90
$COD_{influent}$ (g/L)	3.1 (0.46) n=14	5.8 (1.12) n=13	8.7 (0.90) n=10	10.7 (2.23) n=8	13.0 (8.24) n=3	11.3 (5.09) n=6
COD Loading Rate (g COD/L/d)	2.4 (0.34) n=13	4.5 (0.85) n=13	6.6 (0.68) n=10	8.5 (1.2) n=5	4.8 (3.1) n=3	2.7 (1.4) n=5
$pH_{(effl)}$	6.4 (0.46) n=39	7.1 (0.55) n=43	7.5 (0.16) n=31	6.6 (0.81) n=36	7.0 (0.77) n=10	7.6 (0.28) n=12
COD reduction (%)	48 (18.5) n=14	72 (18.5) n=9	92 (2.3) n=10	49 (18.2) n=8	72 (20.2) n=2	80 (5.6) n=5
Total Volatile Acids (mg/L)	736 (454) n=12	1735 (1350) n=18	271 (93) n=13	2012 (1106) n=18	3031 (1400) n=6	1274 (491) n=5
Total Alkalinity (mg/L)	1084 (290) n=12	2818 (615) n=18	3079 (202) n=13	2336 (446) n=18	3378 (843) n=6	3807 (744) n=5
VA/BA Ratio n=5	3.9 (5.8) n=12	2.6 (3.2) n=18	0.10 (0.04) n=13	3.4 (3.4) n=18	25.3 (42.6) n=6	0.54 (0.31)
* Specific Biogas Production (LCH_4/gCOD added)	0.15	0.13	0.27	0.02	-	-
* Specific Biogas Production (LCH_4/gCOD removed)	0.31	0.18	0.29	0.04	-	-
Methane content (% of volume)	48.6 (11) n=4	53.4 (19.4) n=7	58.2 (9.82) n=8	26.0 (17.1) n=5	-	-
Influent Furfural Concentration (g/L)	-	-	-	-	2.1 (3.2) n=10	5.1 (2.4) n=11
Biogas Production (L/d)	9.9 (8.8) n=39	14.6 (8.3) n=44	43.1 (11) n=32	9.3 (16) n=40	4.4 (6.4) n=10	20.8 (10.7) n=11

* Calculated parameter
n = number of samples
( ) = standard deviation

The specific biogas production for this period increased from 0.03 to 0.31 LCH_4/g COD (removed) for R_2. It, however, stayed at the range of 0.18 to 0.31 for R_3.

Performance of Reactor 3 deteriorated from period 3 to 4. This drop in performance was probably due to the heat tracer malfunction in this unit allowing the temperature of the reactor contents to climb to 39°C on day 136 of operation. This had a detrimental effect on the performance of the methanogenic bacteria as the TVA concentration rose from 271 to 2012 mg/L and the biogas production dropped from 43 to 9 L/d, while the methane content of the biogas dropped from 58 to 26%.

In the furfural addition period, the combination of sudden load increase from an average of 6.5 to 7.7 and the addition of 4.5 g/L furfural (period 4) resulted in a drop in performance as signaled by a drop in COD removal from an average of 89% to 85% and an increase in VA/BA from 0.23 to 16.6. To control the VA/BA ratio, the loading rate was decreased to 3.9 kg COD/m^3·d (period 5) while the furfural concentration was increased to 6 g/L. This resulted in an improved VA/BA ratio even though the average COD reduction dropped to 78%.

For R_3, 2.1 g/L of furfural was added while the COD loading rate was decreased from an average of 8.5 (period 4) to 4.8 kg COD/m^3·d (period 5). This resulted in an increase in the average COD reduction from 49 to 72%, even though the VA/BA ratio increased drastically from 3.4 to 25.3. In period 6, as the COD loading was decreased to 2.7 kg COD/m^3·d, the COD removal increased to 80% and VA/BA dropped to 0.54, while the furfural concentration was increased from 2.1 g/L (period 5) to 5.1 g/L (period 6).

It was observed that acclimatized methanogenic bacteria could tolerate higher levels of furfural at low organic loadings.

Using the performance plots (Figures 6.1 and 6.2) and the performance data (such as those summarized in Tables 6.1 to 6.3), and based on the trends observed for the anaerobic reactors, design criteria were developed for the large-scale implementation of the anaerobic treatment systems. Based on the greater COD removal efficiency at higher organic loadings and the higher tolerance to upset by high furfural

levels of the USB, the USB system was selected for the preliminary process design. Table 6.4 is a summary of the process standards developed in this study. The information given in Table 6.4 formed the basis for the scale-up of the selected anaerobic system outlined in section 7.0.

Table 6.4
DESIGN CRITERIA DEVELOPED FROM THE TREATABILITY STUDY, WASTE CHARACTERIZATION AND LITERATURE REVIEW

Parameter	Design Criteria
Mill size (tonnes wood/day)	1,000
Condensate volume (L/tonne wood processed)	450
$COD_{(infl)}$ (mg/L)	22,500 mg/L
Loading (kg COD/m^3·d)	7
COD reduction (%)	90%
Biogas methane content	60%
Specific biogas production (LCH_4/g COD removed)	0.35
Operating temperature (°C)	35

6.1.2 The Pre-acidification Stage

Addition of the pre-acidification treatment (PAT) stage to the two USB reactors was found to be unnecessary. This finding was based on the comparison of R_1 and R_2 performances after day 126, when the PAT prior to the reactor 2 was removed. The R_2 performance did not deteriorate after the PAT removal and was comparable to the performance of R_1 (which was still equipped with PAT). The observed improvement in performance of the two reactors at the initial stages of PAT installation was, therefore, attributed to the continued acclimation of the anaerobic bacteria to the SEPC feed.

Equalization of the SEPC waste stream may, however, be required in the full-scale operation as the condensate temperature will be well above the optimum (35°C) for the mesophilic methanogenesis.

6.1.3 Furfural Spike Testing

USB reactors R_2 (on day 164) and R_3 (on day 171) were spiked with higher levels of furfural. Organic loadings were also

increased concurrently. The high initial organic loading - furfural concentration combination proved to be detrimental to the digesters' performance. In an attempt to correct the problem, the organic loadings were subsequently lowered. As the reactors' performance returned to normal with the lowered loadings, furfural concentrations were systematically increased.

An incremental increase in the furfural concentration resulted in little or no decrease in performance. It was observed that at lower organic loadings, higher concentrations of furfural (up to 8 g/L) are tolerated by acclimatized microbial population.

6.1.4 Activated Sludge Polishing

Performance of the activated sludge system (started on day 118) improved with time. Start-up problems, such as the poor sludge settling and the resulting impaired microbial activity, gradually improved as the bacterial population responsible for the waste stabilization acclimatized to the new substrate. The activated sludge system's performance continued to improve and approached steady-state conditions with the continued operation of the system at the desired operating conditions.

In comparison to the anaerobic reactors, monitoring the performance of the activated sludge was slightly more difficult as the performance of this aerobic system was dependent on the anaerobic reactors' effluent quality, whose effluents were used as feed for the activated sludge system. The activated sludge system evaluation was conducted concurrently with the furfural spiking experiments on the anaerobic treatment systems. During periods when the anaerobic reactors were upset, the activated sludge system also experienced operational problems as it received higher than desired BOD loadings.

For this reason, the activated sludge system's operational parameters were averaged over the entire monitoring period and the averaged parameters were used in the scale-up design. Table 6.5 lists the average performance of the activated sludge system. The activated sludge system achieved additional post anaerobic BOD reduction of up to 73%, under all conditions tested. A design removal efficiency of 90% is anticipated under steady state conditions.

Table 6.5
ACTIVATED SLUDGE SYSTEM PERFORMANCE

	Average Value
$pH_{infl.}$	7.1
$BOD_{infl.}$ (mg/L)	1693
$BOD_{effl.}$ (mg/L)	221
$BOD_{rem.}$ (%)	74%
$SBOD_{infl.}$ (mg/L)	1431
$SBOD_{effl.}$ (mg/L)	299
$COD_{infl.}$ (mg/L)	3930
$COD_{effl.}$ (mg/L)	813
$COD_{rem.}$ (%)	55%
$SCOD_{infl.}$ (mg/L)	3287
$SCOD_{effl.}$ (mg/L)	618
Load (kg BOD/m^3.d)	3.4
(kg COD/m^3.d)	7.9
SRT (d)	3.7
MLVSS (mg/L)	3928
F/M (g COD/g MLVSS)	1.4
HRT (d)	0.5
SVI (mL/g)	84.8
Q/Q_r	0.25

Satisfactory performance of this aerobic waste stabilization system is indicative of the effectiveness and suitability of the activated sludge process for the treatment of the anaerobic digestion effluents.

6.2 Lignin Recovery Waste ATA Testing

To investigate the possible inhibitory effects of the lignin recovery wastewaters, anaerobic toxicity assay (ATA) tests were set up. Based on the data obtained from the waste characterization, varying concentrations of the wastewater were used. The ATAs were run in triplicate. The volumes of waste selected were 5, 10, 20, 40 and 60% of the total assay volume.

Daily gas production data were collected for each concentration series. Cumulative averaged results were plotted against time. Figure 6.3 is a typical ATA plot. The inhibitory effect of the wastewater was determined by comparing differences in methane production rates in the test units with those in the spiked blanks.

It was observed that the lignin recovery wastewater stimulates growth slightly at low concentrations but is inhibitory at higher concentrations. It was further observed that given sufficient time, higher rates of methane production could be achieved at even higher concentrations. This is attributed to the acclimation of the anaerobic microorganisms to the new substrate.

Using the gas production data for the first 14 days of ATA testing, the coefficient of inhibition for this waste was estimated to be in the 30-40% range. No estimate of the anticipated volume of lignin recovery wastewater is currently available but it will be small in comparison to the total Wood-to-Ethanol wastewater flow and should not result in any operational problems with the full-scale anaerobic system if it is blended with the other waste streams.

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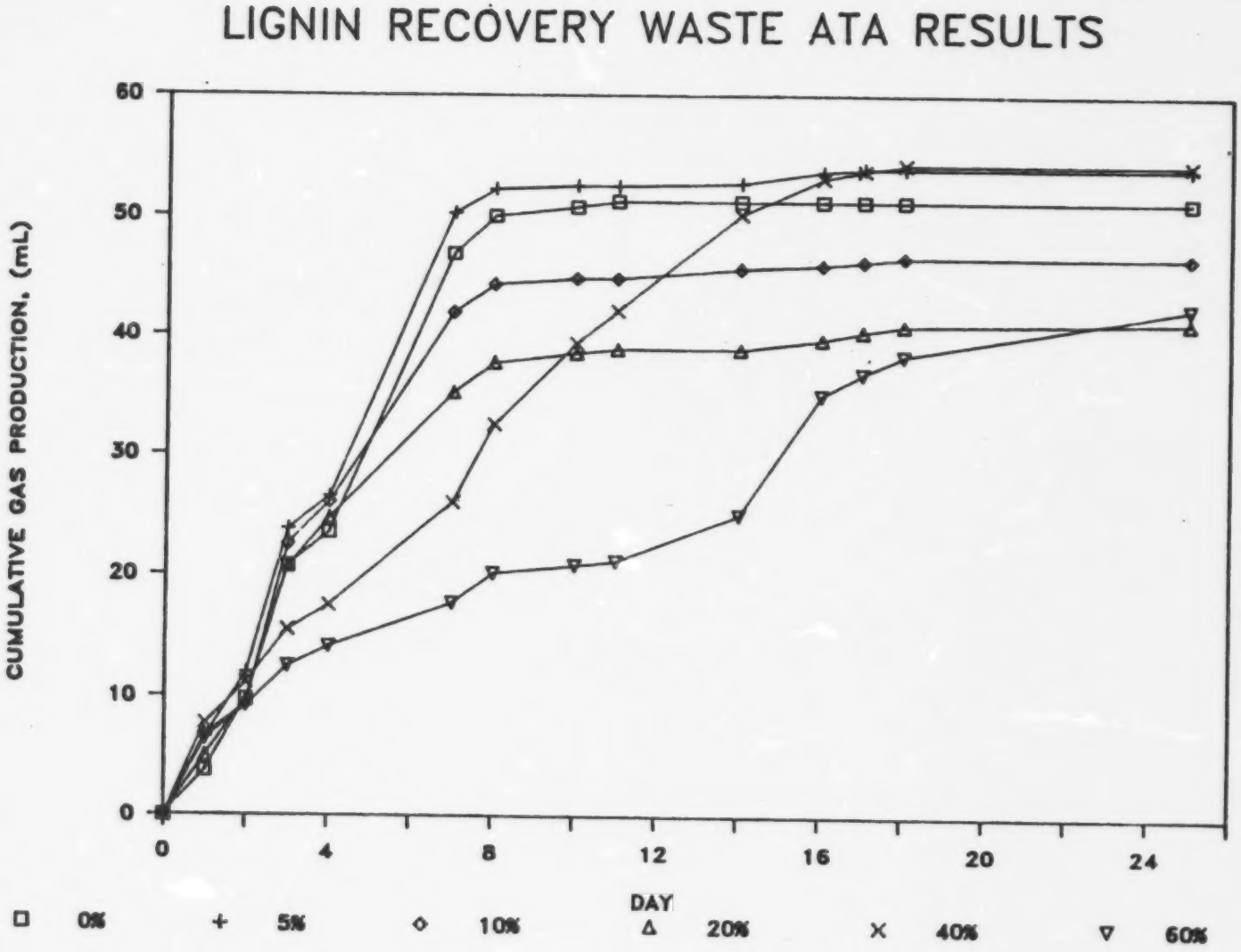

Figure 6.3 A Typical ATA Plot

7.0 PRELIMINARY PROCESS DESIGN

A simplified schematic of the proposed Wood-to-Ethanol plant effluent treatment system is shown in Figure 7.1. The wastewater would be screened as it leaves the Wood-to-Ethanol production facility just prior to entry into the treatment facility. The wastewater would then flow to a flow and concentration equalization tank located at the head of the wastewater treatment plant. The equalization tank would provide a return point for the effluent recycle from the anaerobic treatment unit and the filtrate from the sludge treatment unit. The equalization tank would be mixed using a submersible mixer in order to maintain a uniform wastewater concentration and temperature.

The pH of the wastewater in the equalization tank will be monitored and 50% caustic solution will be metered into the tank as required in order to maintain the target wastewater pH. A target pH of 6.5 would be used during start-up. During the treatment of the wastewater in the anaerobic reactor, bicarbonate alkalinity is produced (approximately 1.3 mg as $CaCO_3$/mg COD destroyed) raising the pH in the reactor and the reactor effluent. As the bacterial seed acclimatizes, the pH of the wastewater would be allowed to drop to reduce caustic demand and a target of greater than pH 4.0 may be maintained.

The equalized wastewater will be pumped at a constant volume through a steam injection system. The steam injection system will use live steam from the ethanol plant to increase the wastewater temperature to the anaerobic reactor operating temperature of 30-35 °C as required. The steam addition will be made using a PID control system.

Micronutrients will be added to the wastewater just prior to discharge into the distribution header of the anaerobic reactor. A micronutrient formula similar to the formula used in the treatability study (Table 5.2) is proposed. After acclimatization a more detailed evaluation of the nutrient requirement would be conducted and the formula adjusted as required.

The anaerobic reactor would be operated in upflow mode with the biogas being recovered for utilization in the ethanol plant boilers or to provide electrical power for the ethanol plant. The effluent would be discharged from the top of the reactor and some would be directed back to the equalization

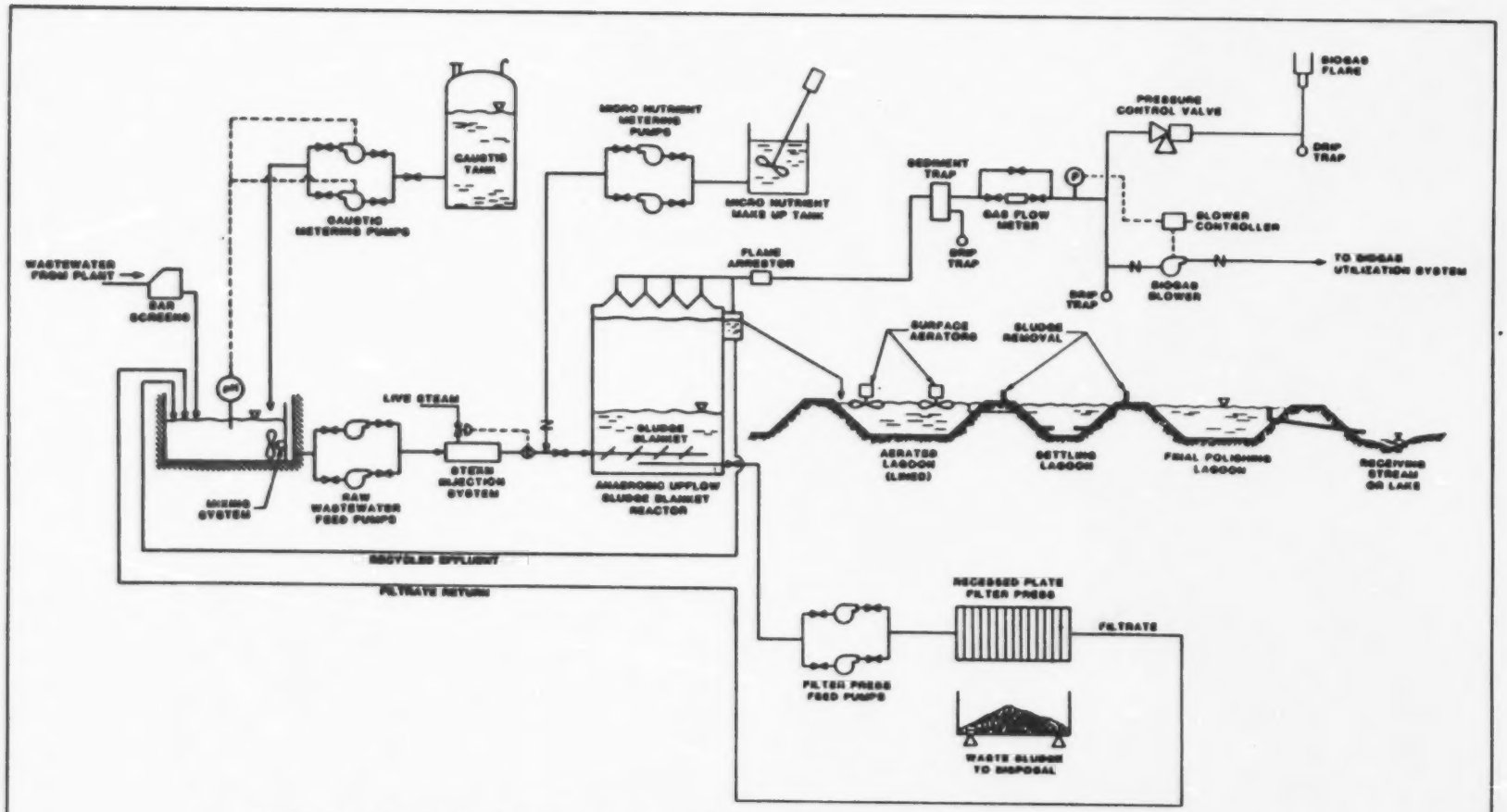

FIGURE 7.1 : SIMPLIFIED SCHEMATIC OF PROPOSED WASTEWATER TREATMENT SYSTEM FOR A 1000 TONNE/DAY WOOD-TO-ETHANOL FACILITY

tank as effluent recycle and the remainder would flow by gravity to the aerated lagoon for additional polishing.

The aerated lagoon could be constructed using concrete, steel or earth. The lined earthen lagoon was selected for this evaluation since it usually represents the most cost effective construction while providing adequate ground water protection.

Aeration of the polishing lagoon can be accomplished using below surface diffusion systems or surface aeration systems. The floating aerated system was used in this evaluation since it is the most cost effective system under normal design conditions. A subsurface diffusion system may be required depending on local climatic conditions. This would increase the capital cost slightly and reduce the operating cost slightly.

A secondary polishing lagoon is provided in the proposed design to provide final polishing of the wastewater prior to discharge to the receiving stream. This final polishing lagoon would be divided into two sections. The first section would provide storage space for the settleable solids that may be contained in the aerated lagoon effluent. These solids would settle and could periodically be removed from this section of the lagoon as required. After the initial settling stage, the effluent would be held in the secondary polishing lagoon for final polishing and then discharged to a receiving stream or surface body of water. The final effluent target criteria would be 30 mg/L of suspended solids, 30 mg/L biochemical oxygen demand, 5 mg/L total nitrogen and 1 mg/L total phosphorus. This level of treatment would allow construction of the plant in most areas in Canada and direct discharge of the treated effluent to most bodies of water in Canada.

The sludge produced in the anaerobic reactor would be withdrawn as required and pumped through a filter press unit to reduce the moisture content. The sludge cake would be sufficiently stabilized and dewatered for disposal on agricultural land or at a sanitary landfill site. The filtrate would be returned to the equalization tank for further treatment.

If the ethanol plant were located in an area where the wastewater could be discharged to a municipal sewer the effluent from the anaerobic unit may be suitable for direct

discharge to the sewer. Therefore, the aerated and polishing lagoons would not be required. This would result in considerable capital and operating cost savings. In most cases the sludge could be utilized on agricultural land. However, if land in the immediate area (usually within 10 km) of the plant is not available then the sludge will need to be dewatered and disposed of to a sanitary landfill.

7.1 Wastewater Treatment Plant Unit Sizing and Energy Balance

During the treatability testing and evaluation phase only two wastewater streams were available in sufficient quantity to be evaluated out of many potential wastewater streams, that may be generated from a typical Wood-to-Ethanol plant. Out of the two streams that were available, only one stream was available in sufficient quantity for pilot testing. The wastewater volume estimates for a Wood-to-Ethanol plant are highly variable and will depend on the final plant configuration. Wastewater volumes and characteristics for the other potential wastewater streams were not available. The steam explosion pretreatment condensate (SEPC) appears to be the waste stream with the highest flow and concentration and therefore will represent the most significant loading to the wastewater treatment facility. For the purpose of this report the wastewater characteristics obtained during this study of the steam explosion condensate were used to size a waste treatment facility for a 1,000 tonnes/d Wood-to-Ethanol facility.

A summary of the design sizing and energy balance is shown in Table 7.1.

A design flow of 450 L/tonne of wood produced is based on the typical condensate flows generated during the steam explosion pilot plant operation for the experimental runs conducted. The condensate COD and BOD_5 levels represent the wastewater strength obtained during the optimum operating temperatures and pressures. Although the suspended solids in the condensate was extremely low an allowance for up to 500 mg/L was made to allow for other high strength solids containing streams that may be combined with the condensate stream in the Wood-to-Ethanol plant effluent. The design temperature of 30 °C was used to allow for some combination of lower temperature waste streams with the condensate stream.

Table 7.1
PROCESS DESIGN SUMMARY FOR CONDENSATE TREATMENT
FROM A 1000 TONNE/DAY WOOD-TO-ETHANOL PLANT

Anaerobic Upflow Sludge Blanket First Stage

Flow	450 m^3/d
BOD_5	15000 mg/L
COD	22500 mg/L
SS	500 mg/L
Wastewater Temperature	30 degrees C
BOD_5 Loading	6750 kg BOD/d
COD Loading	10125 kg COD/d
SS Loading	225 kg SS/d
Design Loading	7 kg COD $m^3 \cdot d$
Digester Size	1446 m^3
Digester Surface Area	223 m^2
Sludge Concentration	40 Kg/m^3
F/M Ratio (COD basis)	0.46
HRT	77 hours
COD Removal Efficiency	90%
BOD_5 Removal Efficiency	90%
SS Removal Efficiency	50%
COD Removed	9113 kg COD removed
BOD_5 Removed	6075 kg BOD_5 removed
SS Removed	113 kg SS removed
SS Growth Coefficient	0.08 kg SS/kg COD
SS Growth	729 kg SS/d
Effluent COD	2250 mg/L
Effluent BOD_5	1500 mg/L
Effluent SS	1870 mg/L
Methane Production	3189 m^3 CH_4/d
Biogas Production	5315 m^3/d
Total Energy Produced	113 GJ/d
Total Energy Required	9.7 GJ/d
Boiler Efficiency	80%
Heat Available from Biogas	100 GJ/d
Excess Heat Energy	80 GJ/d
Energy Cost	3.85 $/GJ
Total Daily Energy Savings if Biogas Utilized	$387 $/day

Table 7.1
(continued)

Aerated Lagoon Second Stage	
Flow	450 m^3/d
BOD_5 (after AD)	1500 mg/L
COD (after AD)	2250 mg/L
SS (after AD)	1870 mg/L
BOD_5 Loading	675 kg/d
BOD_5 Loading Rate	0.10 kg $BOD/m^3 \cdot d$
Volume Required	6750 m^3
Depth	5 m
Surface Area Required	1350 m^2
HRT	15 d
O_2 Requirement	1013 kg O_2/d
Aeration Requirement	48 kW-h/h
Aeration Mixing Per m^3	7 W/m^3
BOD_5 Removal Efficiency	90%
SS Removal Efficiency	50%
Effluent BOD_5	150 mg/L
Effluent SS	935 mg/L
Final Holding Lagoon	
Flow	450 m^3/d
BOD_5 (after aeration)	150 mg/L
SS (after aeration)	935 mg/L
BOD_5 Loading	68 kg/d
BOD_5 Loading Rate	0.0125 kg $BOD/m^3 \cdot d$
Volume Required	5400 m^3
Depth	5 m
Surface Area Required	1100 m^2
HRT	12 d
BOD_5 Removal Efficiency	80%
SS Removal Efficiency	97%
Effluent BOD_5	30 mg/L
Effluent SS	28 mg/L

A total COD loading of 10125 kg/d was used to size the anaerobic reactor. A design loading of 7 kg COD/m^3·d was used for the design. This results in an F/M (Food-to-Microorganism) ratio of 0.5 d^{-1} assuming a sludge concentration of 40 kg/m^3 and an average depth of 2.5 m in the reactor. The recycle flow rate will be quite high (approximately 2300 m^3/d) in order to maintain the appropriate upflow velocity in the anaerobic reactor of between 0.5 m/h and 1.5 m/h. This recycle rate may be reduced considerably if other more dilute waste streams are added to the plant effluent.

The anaerobic treatment plant effluent COD, SS and BOD_5 levels are estimated to be 2250 mg/L, 1870 mg/L and 1500 mg/L, respectively, and are too high for direct discharge to a receiving stream.

The anaerobic reactor will produce approximately 6000 m^3/d of biogas containing approximately 3200 m^3 of methane. The total energy value is estimated at approximately 113 GJ/d. The energy required for the anaerobic reactor is estimated at 13 GJ/d and the excess energy is estimated at 100 GJ/d. The excess energy would be capable of producing 35,000 kg steam/day or producing 9300 kW-hr (ie. 388 kW) of power daily. A daily energy cost savings of $387 could be attained if this energy could be used onsite to fuel plant boilers at a displaced fuel price of $3.85 GJ or approximately $558/d if electrical energy is produced assuming displaced power at $0.06/kW-hr.

The second stage aerated lagoon was designed using a flow of 450 m^3/d and a BOD_5 concentration of 1500 mg/L (after anaerobic digestion). A conservative design loading rate of 0.10 kg BOD/m^3·d was used to size the lagoon. The resulting lagoon volume is about 7250 m^3 and would be approximately 40 m by 40 m in size. Four surface aeration units of 12 kw capacity were used to provide aeration.

The effluent from the first stage aerated lagoon is estimated to contain approximately 150 mg/L of BOD_5 and up to 900 mg/L of SS depending on the initial wastewater suspended solids.

The final holding lagoon is designed in two sections, the first section would be used to settle suspended solids and the second section as a final settling area. The lagoon is designed using a conservative loading of 0.025 kg BOD/m^3·d. The settling section contains 2700 m^3 of wastewater and would be designed for easy removal of sludge and the final

section will contain 2700 m^3 of wastewater and provide natural reaeration of the treatment plant effluent prior to discharge to the receiving stream.

The estimated final effluent would be approximately 30 mg/L BOD_5 and 30 mg/L SS.

7.2 Estimated Full-Scale Costs

An estimate of the total capital cost for the proposed treatment system is summarized in Table 7.2. The capital costs do not include biogas utilization equipment costs.

Table 7.2
ESTIMATED CAPITAL COSTS FOR AN ANAEROBIC TREATMENT SYSTEM FOR PRETREATMENT CONDENSATE FROM A 1000 TONNES/D WOOD TO ETHANOL PLANT

	$ x 1000
Major Component Costs	
Effluent Pumping	$ 75
Pretreatment Equalization	125
Anaerobic Reactors and Instrumentation	1600
Gas Handling and Flare	120
Yard Piping (Allowance)	100
First Stage Aerobic Lagoon	200
Final Holding Lagoon	150
Sludge Dewatering and Control Building	300
Subtotal	2,670
Pilot Testing, Design, Construction and Start-Up	
Preliminary Engineering and Pilot Testing	$ 75
Detailed Engineering and Site Supervision	400
Start-Up Program/Training	40
Contingency (10%) Total Capital Cost	270
Subtotal	$ 785
TOTAL ESTIMATED CAPITAL COST	$3,455

The capital costs were estimated using an installed unit cost method for the major components and actual costs for similar installed systems with price escalation to September 1989 using the Engineering News Record (ENR) construction index.

Since we were unable to evaluate the total plant wastewater from a Wood-to-Ethanol plant, a pilot plant program is included in the capital cost prior to design of a treatment facility.

The total cost including pilot testing, engineering start-up and a 10% Contingency is $3,455,000. This facility would treat approximately 10,000 kg of COD/d or 3,600,000 kg of COD annually and produce 36,500 GJ of excess energy per year.

An estimate of the Annual operating cost for the proposed treatment system is summarized in Table 7.3.

Table 7.3
ESTIMATED OPERATING AND MAINTENANCE COSTS FOR AN ANAEROBIC TREATMENT SYSTEM FOR PRETREATMENT CONDENSATE FROM A 1,000 TONNES/D WOOD-TO-ETHANOL PLANT

	$/y
Equipment Repairs (2% of Capital Cost)	$54,000
Analytical Testing	14,000
Chemical Costs	
Nitrogen (48000 kg/y @ $0.50/kg)	24,000
Phosphorus (4800 kg/y @ $0.75/kg)	3,600
Trace Micro-nutrients (6500 kg/y @ $2.50/kg)	19,500
Caustic (136000 kg/y @$0.50/kg)	68,000
Polymer (Sludge Dewatering) (680 kg/y @ $5/kg)	3,500
Power (650000 kW h @ $0.06/kw-h))	40,000
Other Utilities	20,000
Estimated Subtotal	246,500
Labour Cost	
Supervision and Administration (1d/wk)	15,000
Operational Labour (2 p/y @ $35,000/y)	70,000
Total Estimated Labour Cost	85,000
Total O+M Cost	340,500

The operating costs include a 2% of installed capital cost allowance for repairs and maintenance of the facility. An operating cost for analysis of the plant wastewater and the unit operations is included assuming this analysis is sub-contracted. All regulatory monitoring would be in addition to this cost and varies widely depending on the location in Canada. Chemical costs are based on treating 3,600,000 kg of COD/year using a 750:10:1 COD/nitrogen/phosphorous ratio and a caustic addition rate of 4% of the COD treated.

The micro-nutrient mixture and addition rate as formulated for use in the pilot study was used to estimate the cost of micro-nutrient addition. The polymer addition requirements were based on an estimated 2.5 kg/tonne of solids treated and a solids production level of approximately 8% of the COD treated or 272,000 kg of dry solid/year.

Labour cost is estimated for two full time operators at $35,000/y including benefits and 1 d/wk supervision of operation at $15,000/y including benefits.

The total estimated operating cost is approximately $340,500.

Table 7.4 summarizes the income from the utilization of biogas as a fuel for the plant boilers or to produce electrical power. These calculations both assume that all of the energy can be used onsite by the Wood-to-Ethanol plant. The energy available to the boilers is 36,500 GJ/year resulting in a $140,500 savings if the displaced fuel is $3.85/GJ.

The total operating cost is significantly greater than the estimated savings and therefore no payback is anticipated in the wastewater treatment system.

Table 7.4
ESTIMATED INCOME FROM BIOGAS UTILIZATION

	Option	Savings
1	Fuel Steam Boilers 36500 GJ/y @ $3.85/GJ	$140,500

8.0 REGULATORY ISSUES

Presently in Canada there does not exist an effluent guideline or regulation specific to and directly applicable for the Wood-to-Ethanol Industry. Combinations of the existing Federal and Provincial Legislations may be used.

Both the Federal and Provincial jurisdictions classify various industries into 6 or 7 main industrial groups and target the specific parameters of concern for each industry. Maximum allowable guideline limits for a given parameter may, therefore, vary from industry to industry and from jurisdiction to jurisdiction.

The Wood-to-Ethanol conversion process is carried out in two general stages:

Stage I: Pretreatment/Hydrolysis Stage
Stage II: Fermentation/Distillation Stage

Wastewaters generated in Stage I most closely resemble the pulp and paper industry effluents, while the Stage II waste streams closely approximate the characteristics of the distillery (food industry) wastewaters.

Combinations of the pulp and paper and distillery effluent guidelines may be employed for developing a guideline that would apply to the Wood-to-Ethanol industry effluents. The most stringent limits from the two industries may be selected for this purpose.

In most Canadian jurisdictions (such as Manitoba, Saskatchewan, Quebec, Newfoundland and Nova Scotia) the Federal guidelines will apply. In other provinces (for example, Ontario, British Columbia, Alberta and New Brunswick) where more stringent provincial guidelines exist, the most stringent of the Provincial-Federal guideline limits will be applicable.

For example, for a Wood-to-Ethanol plant in Ontario, the Provincial regulations will likely apply. In Ontario, discharge guidelines are being developed under the Municipal and Industrial strategy for Abatement (MISA) Program. The MISA Program is presently in the pre-regulation monitoring stage and will be enforced in the subsequent regulation monitoring stage.

The guidelines for plants located in other provinces may vary somewhat from the Ontario MISA program. Nonetheless, the MISA guidelines may be used as a typical guideline for designing future wastewater treatment facilities for the Wood-to-Ethanol industry in most other jurisdictions.

9.0 SUMMARY AND CONCLUSIONS

9.1 Treatability Study

The overall objectives of the project were to characterize and assess selected waste streams generated during the processing of sugars derived from lignocellulosic feedstocks to produce fuel grade alcohol and to conduct a comprehensive treatability program to develop process standards for waste treatment, with emphasis on energy recovery and utilization. Based on the findings of an extensive literature review and identification and characterization of waste streams generated during the production of fuel alcohol, two waste streams were selected for treatability or toxicity analysis. In selecting appropriate treatment technologies, an emphasis was placed on the potential for energy recovery and utilization.

A steam explosion pretreatment condensate (SEPC) waste stream was treated anaerobically. Bench-scale USB and fixed film anaerobic flow-through reactors were used. SEPC was found to be anaerobically biodegradable. COD removals of 80-95% were achieved at 8-10 kg COD/m^3·d organic loadings. Batch ATA analysis was performed on a lignin recovery waste stream.

Based on the results of the treatability testing, process standards and design criteria were developed for the full-scale implementation of an anaerobic/aerobic waste treatment system. The overall design included process designs, energy balances, and economic assessments including the estimation of the anticipated capital, operation and maintenance costs.

At the request of Energy, Mines and Resources Canada, a poster was prepared by CH2M HILL describing the objectives, methodology and results of the project. This poster was presented at the Seventh Canadian Bioenergy R&D Seminar in Ottawa (April 24-26, 1989).

The following conclusions may be drawn from the treatability testing conducted on the selected Wood-to-Ethanol wastewaters:

1) Characteristics of the steam explosion pretreatment condensate (SEPC) waste stream varied with the production process operating conditions. COD

of the condensate ranged from 3,000 to 20,000 mg/L.

2) Performance of the flow-through reactors treating the SEPC wastewater improved with time indicating a more stabilized operation at progressively high organic loadings. This is an indication of the progressive acclimation of the anaerobic micro-organisms to SEPC.

3) Full-scale treatment facilities for the SEPC wastewater may be designed for approximately 7 kg COD/m^3·d organic loadings. At these loading rates, COD removals of up to 95% are anticipated.

4) A pre-acidification stage before methanogenesis for the SEPC waste was found to be unnecessary.

5) At lower organic loadings, high concentrations of furfural in the SEPC wastewater (up to 8 g/L) would be tolerated by the acclimated microbial population.

6) Aerobic polishing of the anaerobic digestion effluents for further BOD reduction may be required where effluents are disposed of in surface waters.

7) Activated sludge was found to be suitable for polishing the anaerobic digestion effluents from the SEPC wastewater.

8) COD of the lignin recovery waste stream was lower in comparison. COD of this wastewater measured 4,500 mg/L.

9) The lignin recovery waste was found to stimulate growth at low concentrations but is inhibitory to methanogenesis at higher concentrations. The inhibition coefficient was found to be in the 30-40% range.

9.2 Full-Scale Cost Estimate

Projected capital and O&M costs were estimated, and estimates of revenue/savings were developed for a full-scale

wastewater treatment system. The following is a summary of the estimated costs:

1) The total estimated operating cost is approximately $340,500 annually. This includes chemicals, repairs and maintenance and labour costs.

2) The total capital cost including the recommended pilot testing, engineering, start-up assistance, operator training and a 10% contingency is $3,455,000. The capital costs do not include biogas utilization.

3) The income from the utilization of biogas as a fuel for the plant boilers or to produce electrical power is significantly lower than the estimated total operating cost. No payback is, therefore, anticipated in the wastewater treatment system.

10.0 RECOMMENDATIONS

The following recommendations are made based on the information obtained during this study:

1) A detailed mass balance with respect to wastewater production and characteristics from the Wood-to-Ethanol process should be made in terms of wastewater parameters (such as COD, BOD, nitrogen, phosphorus, etc). This study should concentrate on developing a total wastewater flow and typical wastewater characteristics.

2) A pilot study should be conducted when sufficient quantities of the total plant (Wood-to-Ethanol) wastewater is available.

3) Discussions with Environment Canada and the Provincial Ministries of Environment should be initiated to establish the effluent requirements and monitoring programs that will be required for a full-scale Wood-to-Ethanol plant.

4) Wastewater treatment of Wood-to-Ethanol plant effluents will add to the capital and operating costs of the plant and should be considered in the overall economic feasibility of the plant.

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